

Long-range corrected hybrid meta-generalized-gradient approximations with dispersion corrections

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We propose a long-range corrected hybrid meta-GGA functional, based on a global hybrid meta-GGA functional, M05 [Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Phys.* **123**, 161103 (2005)], and empirical atom-atom dispersion corrections. Our resulting functional, ω M05-D, is shown to be accurate for a very wide range of applications, such as thermochemistry, kinetics, noncovalent interactions, equilibrium geometries, frontier orbital energies, fundamental gaps, and excitation energies. In addition, we present three new databases, IP131 (131 ionization potentials), EA115 (115 electron affinities), and FG115 (115 fundamental gaps), consisting of experimental molecular geometries and accurate reference values, which will be useful in the assessment of the accuracy of density functional approximations.

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I. INTRODUCTION

Because of its satisfactory accuracy and modest cost in many applications, Kohn-Sham density functional theory (KS-DFT) [1, 2] has become one of the most popular electronic structure methods for large ground-state systems [3–6]. Its extension for treating excited-state systems, time-dependent density functional theory (TDDFT) [7, 8], has also been widely used.

The crucial ingredient of KS-DFT, the exact exchange-correlation (XC) energy functional $E_{xc}[\rho]$, however, remains unknown and needs to be approximated. Functionals based on the local density approximation (LDA), modeling the XC energy density locally with that of a uniform electron gas (UEG), have been quite successful for nearly-free electron systems [3, 4], though still insufficiently accurate for most quantum chemical applications. Functionals based on the generalized gradient approximations (GGAs), additionally incorporating the gradient of local density into the LDA, have achieved reasonable accuracy in many applications. As an extension of the GGA (for rather restricted set of density variables), meta-GGA (MGGA) offers itself quite naturally. Functionals depending directly on the Laplacian of the density have not been pursued intensively, because of the difficulty of numerical evaluation. MGGAs, which adopt the kinetic energy density as a substitute for the Laplacian, have shown evidences of superiority over GGAs. [9–11]

However, the LDA, GGAs and MGGAs (commonly denoted as DFAs for density functional approximations) are based on the localized model XC holes, while the exact XC hole should be fully nonlocal. Currently, perhaps the most successful approaches to taking into account the nonlocality of XC hole are provided by hybrid DFT methods, incorporating a fraction of the exact Hartree-Fock (HF) exchange into the DFAs. Hybrid density functionals have achieved remarkable accuracy and have expanded the usefulness of DFT for many applications. Noticeably, global hybrid MGGA functionals [12–20], where the XC energy density depends on the local density, the gradient of local density, a fraction of exact exchange, as well as the exact KS kinetic energy density (a function of the occupied KS orbitals) [21–24], have been shown to potentially perform better than global hybrid GGA functionals [15–20, 25, 26], due to the additional ingredient of kinetic energy density in global hybrid MGGA functionals.

In global hybrid functionals, a small fraction of the exact HF exchange is added to a semilocal density functional. In certain situations, especially in the asymptotic regions of molecular systems, a large fraction (even 100%) of HF exchange is needed. Aiming to remedy this, long-range corrected (LC) hybrid DFT schemes have been actively developed [27–37]. LC hybrids retain the full HF exchange only for the long-range electron-electron interactions, and thereby resolve a significant part of the self-interaction problems associated with global hybrid functionals.

On the other hand, the development of accurate short-range (SR) exchange density functionals $E_x^{\text{SR}}[\rho]$, plays an important role in the progress of LC-DFT. In the first LC scheme, an ansatz for the conversion of any E_x to E_x^{SR} was proposed by Iikura *et al.* [27], and has become widely used. However, their resulting LC hybrid GGA functionals

do not outperform the corresponding global hybrid GGA functionals for thermochemistry. In 2006, Vydrov *et al.* proposed a different LC scheme [31], based on integrating a GGA model exchange hole. Their resulting LC- ω PBE functional has shown improved performance for thermochemistry and barrier heights, and is comparable to global hybrid GGA functionals such as B3LYP [38, 39]. However, further improvements following this direction require the development of more accurate model exchange holes, which is a quite challenging task.

Another approach to more accurate LC hybrid functionals was proposed by Chai and Head-Gordon [35]. First, augmenting the SR local spin density exchange energy density by a flexible enhancement factor (of the Becke’s 1997 form [40]) and fully reoptimizing the LC functional on a diverse training set, yields the ω B97 functional. Second, including an adjustable fraction of SR HF exchange in the ω B97 functional with the similar reoptimization procedure, leads to the ω B97X functional. ω B97 and ω B97X have been shown to be accurate across a diverse set of test data, containing thermochemistry, kinetics, and noncovalent interactions [35].

However, problems associated with the lack of nonlocality of the DFA correlation hole, such as the lack of dispersion interactions (the missing of van der Waals forces), are not resolved by the LC hybrid schemes. The correlation functionals in typical LC hybrids are treated semilocally, which cannot capture the long-range (LR) correlation effects [41, 42]. To remedy this, the DFT-D scheme was applied [43] to extend the ω B97X functional with damped atom-atom dispersion corrections, denoted as ω B97X-D [36]. Consequently, ω B97X-D can obtain dispersive effects with essentially zero additional computational cost relative to ω B97X. As an alternative approach, ω B97X has also been combined with the double-hybrid methods [44–48], which mix both the HF exchange and nonlocal orbital correlation energy from the second-order perturbation energy expression in wave function theory. The resulting ω B97X-2 functional [37] has yielded very high accuracy for thermochemistry, kinetics, and noncovalent interactions, though its fifth-order scaling with respect to system size may limit its applicability to larger systems.

As the ω B97 series are LC hybrid GGAs, it seems a natural step to develop LC hybrid MGGA and to assess their performance. In this work, we propose a new LC hybrid MGGA-D functional, denoted as ω M05-D, which is shown to be accurate for a wide range of applications, when compared with the two closely related functionals: a global hybrid MGGA functional (M05-2X) [19] and a LC hybrid GGA-D functional (ω B97X-D) [36]. The rest of this paper is organized as follows. In Sec. II, we briefly describe the relevant schemes developed in the LC hybrid approach. In Sec. III, we propose a new SR exchange functional, which serves as suitable basis functionals for systematically generating accurate LC hybrid MGGA functionals. The performance of the ω M05-D functional is compared with other functionals in Sec. IV (on the training set), and in Sec. V (on some test sets). In Sec. VI, we give our conclusions.

II. RATIONALES OF LC HYBRID SCHEMES

For the LC hybrid schemes, one first defines the long-range and short-range operators to partition the Coulomb operator. The most popular type of splitting operator used is the standard error function (erf),

$$\frac{1}{r_{12}} = \frac{\text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erfc}(\omega r_{12})}{r_{12}}, \quad (1)$$

where $r_{12} \equiv |\mathbf{r}_{12}| = |\mathbf{r}_1 - \mathbf{r}_2|$ (atomic units are used throughout this paper). On the right hand side of Eq. (1), the first term is long-ranged, while the second term is short-ranged. The parameter ω defines the range of these operators.

In this work, we employ the erf/erfc partition, and use the following expression (as suggested in the recent LC hybrid schemes [35, 36, 49]) for the LC hybrid functionals (c_x is a fractional number to be determined):

$$E_{xc}^{\text{LC-DFA}} = E_x^{\text{LR-HF}} + c_x E_x^{\text{SR-HF}} + (1 - c_x) E_x^{\text{SR-DFA}} + E_c^{\text{DFA}}, \quad (2)$$

where $E_x^{\text{LR-HF}}$, the LR HF exchange, is computed by the occupied KS orbitals $\psi_{i\sigma}(\mathbf{r})$ with the LR operator,

$$E_x^{\text{LR-HF}} = -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{\text{occ.}} \iint \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{j\sigma}^*(\mathbf{r}_2) \frac{\text{erf}(\omega r_{12})}{r_{12}} \psi_{j\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

$E_x^{\text{SR-HF}}$, the SR HF exchange, is computed similarly to the above but with the SR operator,

$$E_x^{\text{SR-HF}} = -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{\text{occ.}} \iint \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{j\sigma}^*(\mathbf{r}_2) \frac{\text{erfc}(\omega r_{12})}{r_{12}} \psi_{j\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

$E_x^{\text{SR-DFA}}$ is the SR exchange approximated by DFAs, and E_c^{DFA} is the correlation functional the same as that of the full Coulomb interaction.

In view of the $E_{xc}^{\text{LC-DFA}}$ in Eq. (2), as $E_x^{\text{LR-HF}}$ and $E_x^{\text{SR-HF}}$ are well defined, and accurate approximations for E_c^{DFA} are widely available, the accuracy of $E_x^{\text{SR-DFA}}$ is thus closely related to the accuracy of a LC hybrid functional [35, 36]. The analytical form of the SR LDA (the simplest SR DFA) exchange functional $E_x^{\text{SR-LDA}}$ can be obtained by the integration of the square of the LDA density matrix with the SR operator [50],

$$E_x^{\text{SR-LDA}} = \sum_{\sigma} \int e_{x\sigma}^{\text{SR-LDA}}(\rho_{\sigma}) d\mathbf{r}. \quad (5)$$

Here, $e_{x\sigma}^{\text{SR-LDA}}(\rho_{\sigma})$ is the SR LDA exchange energy density for σ -spin,

$$e_{x\sigma}^{\text{SR-LDA}}(\rho_{\sigma}) = e_{x\sigma}^{\text{LDA}} F(a_{\sigma}), \quad (6)$$

where

$$e_{x\sigma}^{\text{LDA}}(\rho_{\sigma}) = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \rho_{\sigma}^{4/3}(\mathbf{r}) \quad (7)$$

is the LDA exchange energy density for σ -spin, $k_{F\sigma} \equiv (6\pi^2\rho_\sigma(\mathbf{r}))^{1/3}$ is the local Fermi wave vector, and $a_\sigma \equiv \omega/(2k_{F\sigma})$ is a dimensionless parameter controlling the value of the attenuation function $F(a_\sigma)$,

$$F(a_\sigma) = 1 - \frac{8}{3}a_\sigma \left[\sqrt{\pi} \operatorname{erf}\left(\frac{1}{2a_\sigma}\right) - 3a_\sigma + 4a_\sigma^3 + (2a_\sigma - 4a_\sigma^3) \exp\left(-\frac{1}{4a_\sigma^2}\right) \right]. \quad (8)$$

To develop a possible SR DFA exchange functional $E_x^{\text{SR-DFA}}$ based on the knowledge of a DFA exchange functional E_x^{DFA} , there are three schemes as follows. Consider the general expression of DFA exchange functional, which is

$$E_x^{\text{DFA}} = \sum_\sigma \int e_{x\sigma}^{\text{LDA}}(\rho_\sigma) F_{x\sigma}^{\text{DFA}} d\mathbf{r}, \quad (9)$$

$F_{x\sigma}^{\text{DFA}}$ is the DFA enhancement factor for σ -spin. Depending on the type of DFA, $F_{x\sigma}^{\text{DFA}} = 1$ for a LDA, $F_{x\sigma}^{\text{DFA}} = F_{x\sigma}^{\text{GGA}}(\rho_\sigma, \nabla\rho_\sigma)$ for a GGA, $F_{x\sigma}^{\text{DFA}} = F_{x\sigma}^{\text{MGGA}}(\rho_\sigma, \nabla\rho_\sigma, \tau_\sigma)$ for a meta-GGA, where $\rho_\sigma(\mathbf{r})$ is the spin density, $\nabla\rho_\sigma(\mathbf{r})$ is the spin density gradient, and

$$\tau_\sigma = \frac{1}{2} \sum_i^{\text{occ.}} |\nabla\psi_{i\sigma}|^2 \quad (10)$$

is the spin kinetic energy density.

The first scheme was proposed by Ikura, Tsuneda, Yanai, and Hirao (ITYH) [27, 28, 33], where $E_x^{\text{SR-DFA}}$ can be obtained by substituting a modified Fermi wave vector,

$$k_\sigma = \frac{k_{F\sigma}}{\sqrt{F_{x\sigma}^{\text{DFA}}}} \quad (11)$$

into SR exchange energy density of Eq. (6), which *a priori* produces $E_x^{\text{SR-DFA}}$ from any E_x^{DFA} , and reduces nicely to $E_x^{\text{SR-LDA}}$ from a E_x^{LDA} . Although the ITYH scheme possesses an admirable simplicity, some of its deficiencies (which potentially limit its accuracy) have been found [51].

The second scheme was proposed by Vydrov, Heyd, Krukau, and Scuseria (VHKS) [31, 32], where for a given spherically-averaged exchange hole $h_x^{\text{DFA}}(\mathbf{r}, r_{12})$, $E_x^{\text{SR-DFA}}$ is evaluated as

$$E_x^{\text{SR-DFA}} = 2\pi \int \rho(\mathbf{r}) d\mathbf{r} \int_0^\infty \operatorname{erfc}(\omega r_{12}) h_x^{\text{DFA}}(\mathbf{r}, r_{12}) r_{12} dr_{12}. \quad (12)$$

The pivot of this scheme is the engineering of the DFA exchange hole. The GGA model exchange hole of Ernzerhof and Perdew [52] (EP) provides a framework for modeling any GGA exchange hole. It has made considerable appearances in real applications after parametrization to reproduce the Perdew, Burke, and Ernzerhof (PBE) GGA [53]. In 2008, Henderson, Janesko, and Scuseria [51] (HJS) proposed another general model for the spherically averaged exchange hole corresponding to a GGA exchange functional, based on the work of EP. The HJS model improves upon the EP model by precisely reproducing the energy of the parent GGA, and by enabling fully analytic evaluation of range-separated hybrid density functionals. For meta-GGA, the TPSS exchange and correlation hole

models have been “reverse-engineered” [54]. However, the resulting LC-TPSS functional (a LC hybrid MGGA) has no satisfactory long-range correction effect [31].

The third scheme was proposed by Chai and Head-Gordon (CHG) [35, 36], where $E_x^{\text{SR-DFA}}$ is evaluated as

$$E_x^{\text{SR-DFA}} = \sum_{\sigma} \int e_{x\sigma}^{\text{SR-LDA}}(\rho_{\sigma}) F_{x\sigma}^{\text{DFA}} d\mathbf{r}. \quad (13)$$

This simple scheme is expected to work well for a small ω . For highly parametrized E_x^{DFA} , such as the B97 [40], M05 [18], and M08 [26] functionals, the CHG scheme is particularly attractive due to its simplicity. However, how large is not too large for the ω suitable for the CHG scheme? In the following sections, we will compare the performance of two new LC hybrid MGGA-D functionals, where one is developed by the CHG scheme, while the other is developed by a new scheme provided in this work, and our results help to answer the above question.

III. LC HYBRID MGGA-D FUNCTIONALS

In this section, we introduce our new LC hybrid MGGA-D functionals. Note that LC-TPSS has been developed by utilizing the TPSS exchange hole (based on the VHKs scheme) [31], but it is found that LC-TPSS does not benefit much by admixture of HF exchange. The M11 functional [49] has been developed based on the extension of a global hybrid MGGA functional, M08 [26], to LC-DFT, following the CHG scheme [35].

Parallel to the strategy of the ω B97 series [35, 36], we choose to modify the M05 functional. The M05 functional is a global hybrid MGGA functional with a powerful form [18, 19], and our work is based on modifying this functional. Its exchange part consists of the PBE exchange functional and a reasonable kinetic-energy-density enhancement factor. The PBE exchange is a theoretically sound starting point because it satisfies the correct UEG limit and also has reasonable behavior at large values of the reduced spin density gradient s_{σ} .

To satisfy the UEG limit of SR exchange, we replace the PBE exchange energy density $e_{x\sigma}^{\text{PBE}}(\rho_{\sigma}, \nabla\rho_{\sigma})$ with the SR-PBE exchange energy density $e_{x\sigma}^{\text{SR-PBE}}(\rho_{\sigma}, \nabla\rho_{\sigma})$ generated by the HJS model exchange hole (based on the VHKs scheme), whose virtues are indicated in Sec. II. To achieve a flexible functional form, we retain the kinetic-energy-density enhancement factor (similar to the CHG scheme). We denote this resulting functional as SR-M05 (short-range M05) exchange, as it reduces to the M05 exchange at $\omega = 0$.

$$E_x^{\text{SR-M05}} = \sum_{\sigma} \int e_{x\sigma}^{\text{SR-PBE}}(\rho_{\sigma}, \nabla\rho_{\sigma}) f(w_{\sigma}) d\mathbf{r}, \quad (14)$$

where $f(w_{\sigma})$ is the kinetic-energy-density enhancement factor,

$$f(w_{\sigma}) = \sum_{i=0}^m a_i w_{\sigma}^i. \quad (15)$$

w_σ is a function of t_σ , and t_σ is a function of the kinetic energy density τ_σ of electrons with spin σ , as designed by Becke [23],

$$w_\sigma = (t_\sigma - 1)/(t_\sigma + 1), \quad (16)$$

where

$$t_\sigma = \tau_\sigma^{\text{LDA}}/\tau_\sigma, \quad (17)$$

$$\tau_\sigma^{\text{LDA}} \equiv \frac{3}{10}(6\pi^2)^{2/3}\rho_\sigma^{5/3}. \quad (18)$$

In general, the enhancement factor should be ω -dependent. But from the works of LC-TPSS [31] and M11 [49], the optimal ω for a LC hybrid MGGA is expected to be small as well. For a sufficiently small ω value, our proposed functional form, inspired by the VHKs and CHG schemes, should be a good approximation.

We use the same form for the correlation functional as the M05 correlation functional, which can be decomposed into same-spin $E_{c\sigma\sigma}^{\text{M05}}$ and opposite-spin $E_{c\alpha\beta}^{\text{M05}}$ components,

$$E_c^{\text{M05}} = \sum_\sigma E_{c\sigma\sigma}^{\text{M05}} + E_{c\alpha\beta}^{\text{M05}}. \quad (19)$$

For the opposite-spin terms,

$$E_{c\alpha\beta}^{\text{M05}} = \int e_{c\alpha\beta}^{\text{LDA}} g_{\alpha\beta}(s_{av}^2) d\mathbf{r}, \quad (20)$$

$$g_{\alpha\beta}(s_{av}^2) = \sum_{i=0}^n c_{\alpha\beta,i} u_{\alpha\beta}^i, \quad (21)$$

$$u_{\alpha\beta} = \frac{\gamma_{\alpha\beta} s_{av}^2}{1 + \gamma_{\alpha\beta} s_{av}^2}, \quad (22)$$

$$\gamma_{\alpha\beta} = 0.0062, \quad (23)$$

$$s_{av}^2 = \frac{1}{2}(s_\alpha^2 + s_\beta^2), \quad (24)$$

and for the same-spin terms,

$$E_{c\sigma\sigma}^{\text{M05}} = \int e_{c\sigma\sigma}^{\text{LDA}} g_{\sigma\sigma}(s_\sigma^2) \left(1 - \frac{\tau_\sigma^{\text{W}}}{\tau_\sigma}\right) d\mathbf{r}, \quad (25)$$

$$g_{\sigma\sigma}(s_\sigma^2) = \sum_{i=0}^n c_{\sigma\sigma,i} u_{\sigma\sigma}^i, \quad (26)$$

$$u_{\sigma\sigma} = \frac{\gamma_{\sigma\sigma} s_\sigma^2}{1 + \gamma_{\sigma\sigma} s_\sigma^2}, \quad (27)$$

$$\gamma_{\sigma\sigma} = 0.06. \quad (28)$$

$1 - \tau_\sigma^{\text{W}}/\tau_\sigma$ is a self-interaction correction factor proposed by Becke, [22] in which τ_σ^{W} is the von Weizsäcker kinetic energy density [55] given by

$$\tau_\sigma^{\text{W}} = \frac{|\nabla\rho_\sigma|^2}{8\rho_\sigma}. \quad (29)$$

In a one-electron case, $\tau_\sigma = \tau_\sigma^W$, so Eq. (25) vanishes in any one-electron system. The correlation energy densities $e_{c\alpha\beta}^{\text{LDA}}$ and $e_{c\sigma\sigma}^{\text{LDA}}$ are derived from the Perdew-Wang parametrization of the LDA correlation energy [56], using the approach of Stoll *et al.* [57],

$$e_{c\alpha\beta}^{\text{LDA}}(\rho_\alpha, \rho_\beta) = e_c^{\text{LDA}}(\rho_\alpha, \rho_\beta) - e_c^{\text{LDA}}(\rho_\alpha, 0) - e_c^{\text{LDA}}(0, \rho_\beta), \quad (30)$$

$$e_{c\sigma\sigma}^{\text{LDA}} = e_c^{\text{LDA}}(\rho_\sigma, 0). \quad (31)$$

Based on the above functional expansions, we propose a new LC hybrid MGGA functional, $\omega\text{M05-D}$. It contains a fraction of the SR HF exchange,

$$E_{xc}^{\omega\text{M05-D}} = E_x^{\text{LR-HF}} + c_x E_x^{\text{SR-HF}} + E_x^{\text{SR-M05}} + E_c^{\text{M05}}. \quad (32)$$

We enforce the exact UEG limit for the $\omega\text{M05-D}$ functional by imposing the following constraints:

$$c_{\sigma\sigma,0} = 1, \quad (33)$$

$$c_{\alpha\beta,0} = 1, \quad (34)$$

and

$$a_0 + c_x = 1. \quad (35)$$

Following the general form of the DFT-D scheme [43], our total energy

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (36)$$

is computed as the sum of a KS-DFT part and an empirical atomic-pairwise dispersion correction. We choose to use the same form of unscaled dispersion correction as implemented in $\omega\text{B97X-D}$ [36],

$$E_{\text{disp}} = - \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}), \quad (37)$$

where N_{at} is the number of atoms in the system, C_6^{ij} is the dispersion coefficient for atom pair ij , and R_{ij} is an interatomic distance. The damping function,

$$f_{\text{damp}}(R_{ij}) = \frac{1}{1 + a(R_{ij}/R_r)^{-12}} \quad (38)$$

enforces the conditions of zero dispersion correction at short interatomic separations and correct asymptotic pairwise vdW potentials. Here, R_r is the sum of vdW radii of the atomic pair ij , and the only non-linear parameter, a , controls the strength of dispersion corrections.

To achieve an optimized functional for well-balanced performance across typical applications, we use the same diverse training set described in Ref. [35], which contains 412 accurate experimental and accurate theoretical results, including the 18 atomic energies from the H atom to the Ar atom [58], the atomization energies of the G3/99 set (223 molecules) [59–61], the ionization potentials (IPs) of the G2-1 set [62] (40 molecules, excluding $\text{SH}_2(^2\text{A}_1)$ and $\text{N}_2(^2\Pi)$ cations due to the known convergence problems for semilocal density functionals [60]), the electron affinities (EAs) of the G2-1 set (25 molecules), the proton affinities (PAs) of the G2-1 set (8 molecules), the 76 barrier heights of the NHTBH38/04 and HTBH38/04 sets [15, 63], and the 22 noncovalent interactions of the S22 set [64]. The S22 data is weighted ten times more than the others. All the parameters in $\omega\text{M05-D}$ are determined self-consistently by a least-square fitting procedure described in Ref. [35]. For the non-linear parameter optimization, we focus on a range of possible ω values (0.0, 0.1, 0.2, 0.3, and 0.4 Bohr^{-1}), and optimize the corresponding a values in the steps described in Ref. [36].

M05 and M05-2X [18, 19] both used $m=11$ in Eq. (15) and $n=4$ in Eqs. (21) and (26). However, during the optimization procedure of $\omega\text{M05-D}$, we found that the statistical errors are close for $m=10$ and $m=11$, while the one with $m=11$ has parameters significantly larger. A recent study by Wheeler and Houk has shown that large magnitude of the parameters in Eq. (15) may result in large grid errors [65]. Moreover, the use of large parameters increases the possibility of convergence difficulty as well as the over-fitting effects. Thus, we choose $m=10$ instead of 11 in Eq. (15). The optimized parameters of the $\omega\text{M05-D}$ functional are given in Table I, in which the ω value is same as that of $\omega\text{B97X-D}$, while the fraction of SR HF exchange, c_x , is larger than that of $\omega\text{B97X-D}$ (≈ 0.22). This helps to reduce the self-interaction error (SIE) of the functional, as can be seen in Sec. V.

We also tried a simple model (based on the CHG scheme), where the SR-PBE exchange energy density $e_{x\sigma}^{\text{SR-PBE}}(\rho_\sigma, \nabla\rho_\sigma)$ used in Eq. (14) is substituted with $e_{x\sigma}^{\text{SR-LDA}}(\rho_\sigma)F_x^{\text{PBE}}(s_\sigma)$, that is, the SR LDA exchange energy density in Eq. (6) multiplied by the PBE enhancement factor. We tried this because the mathematical form of the latter is significantly simpler than that of the former, and is the model on which M11 based. The parametrization is the same for this simple model, which we denoted by $\omega\text{M05s-D}$. Compared to $\omega\text{M05-D}$, the optimal ω value is also 0.2 bohr^{-1} , but the corresponding optimal a value is found to be 100 and the linear parameters are also larger.

IV. RESULTS FOR THE TRAINING SET

All calculations are performed with a development version of Q-CHEM 3.2 [66]. Spin-restricted theory is used for singlet states and spin-unrestricted theory for others, unless noted otherwise. For the binding energies of the weakly bound systems, the counterpoise correction [67] is employed to reduce basis set superposition error (BSSE).

Results for the training set are computed using the 6-311++G(3df,3pd) basis set with the fine grid, EML(75,302),

TABLE I. Optimized parameters for ω M05-D. Here, the non-linear parameter a is defined in Eq. (38), and others are defined in Eq. (32)

a	30.0		
ω	0.2 Bohr ⁻¹		
c_x	0.369592		
i	a_i	$c_{\alpha\beta,i}$	$c_{\sigma\sigma,i}$
0	0.630408	1.00000	1.00000
1	-0.219121	-0.95491	-5.26863
2	-0.14411	12.138	17.9935
3	1.27732	-35.1041	-17.6408
4	-1.59959	19.5804	0.625687
5	-5.94702		
6	13.5822		
7	10.5048		
8	-28.7168		
9	-6.89761		
10	19.0574		

consisting of 75 Euler-Maclaurin radial grid points [68] and 302 Lebedev angular grid points [69]. The error for each entry is defined as error = theoretical value – reference value. The notation used for characterizing statistical errors is as follows: mean signed errors (MSEs), mean absolute errors (MAEs), root-mean-square (rms) errors, maximum negative errors (Max(-)), and maximum positive errors (Max(+)).

First, we show the results of the first iteration of fitting procedure, comparing the new LC scheme with the CHG scheme (the simple model) for $\omega=0.1, 0.2, 0.3$ and 0.4 bohr⁻¹. We optimize ω M05 and ω M05s using the corresponding ω PBE and ω PBEs orbitals, and denote these optimized functionals as ω M05* and ω M05s*. The statistical errors are believed to be quite close to those obtained self-consistently. As can be seen in Table II, the difference between the performance of ω M05* and ω M05s* is noticeable for $\omega=0.2$ bohr⁻¹, and becomes larger for a larger ω value. Therefore, a LC hybrid MGGA functional with a larger ω value (such as M11 with $\omega=0.25$ bohr⁻¹) may perform better with our new scheme than with the CHG scheme.

In subsequent iterations, we include the dispersion corrections, increase the training weight of S22 set, and found the functionals optimized with $\omega=0.2$ bohr⁻¹. To view the effect of the long-range correction and the dispersion

corrections, we also consider the functional form M05 and M05-D. The latter is the limiting case where $\omega=0$ for ω M05-D, of which the corresponding optimal a value is found to be 2. We reoptimize M05 and M05-D functionals on the same training set using the M05-2X orbitals, truncate their functional expansions at the same orders $m=10$ and $n=4$, and denote these two reoptimized functionals as M05* and M05-D*. Just like the ω B97X functional without dispersion correction, all data in the training set are equally weighted in the least-squares fitting for M05*.

The overall performance of our new ω M05-D is compared with the trial simple model ω M05s-D, M05-D*, M05* and M05-2X [19], as well as existing ω B97X-D (a LC hybrid GGA-D) [36]. Note that M05 [18] and M05-2X share the same functional form, but the former is distracted to deal with transition-metal compounds, so the latter should be our concern. In the ω B97 series, ω B97X-D has the closest relationship to ω M05-D, while ω B97 and ω B97X, developed without dispersion corrections, are expected to perform poorly for noncovalent interactions.

In Table III, the first comparison (ω M05-D vs. ω M05s-D) partially determines the choice of our proposed functional. Although ω M05-D performs worse than ω M05s-D for HTBH, the overall performance of ω M05-D in the training set is the best.

A second comparison between ω M05-D and M05-D* indicates that the exact long-range exchange indeed leads to an overall improvement to MGGA, although not as large as that to GGA [31, 35, 36]. The third comparison is between M05-D* and M05*. The cooperation of the training weight and the empirical dispersion corrections leads to a significant improvement in the results for noncovalent interactions (the S22 data) and a modest overall change. Recently, there have been the updated reference values for the S22 set [70]. We have also examined the performance of ω M05-D against the updated S22 reference values. As shown in the supplementary material [71], the overall performance of the functional against the updated reference values is similar to that against the original ones.

V. RESULTS FOR THE TEST SETS

To test the performance of ω M05-D outside its training set, we also evaluate its performance on various test sets involving 48 atomization energies in the G3/05 test set [72], 30 chemical reaction energies taken from the NHTBH38/04 and HTBH38/04 databases [15, 63], 29 noncovalent interactions [63, 64], 166 optimized geometry properties of covalent systems [73], 12 intermolecular bond lengths [64], 4 dissociation curves of symmetric radical cations as well as three new databases, consisting of 131 vertical IPs, 115 vertical EAs and 115 fundamental gaps. For excitation energies, we perform TDDFT calculations for 19 valence excitation energies, 23 Rydberg excitation energies and one long-range charge transfer excitation curve of two well-separated molecules. Each EA can be evaluated by two different ways, and each fundamental gap can be evaluated by three different ways, so there are a total of 1038 pieces of data in the test sets, which are larger and more diverse than the training set. Unspecified

TABLE II. Comparisons between the ω M05* and ω M05s* functionals (defined in the text) for different ω values. Statistical errors are in kcal/mol.

	ω (Bohr ⁻¹)	0.1	0.1	0.2	0.2	0.3	0.3	0.4	0.4
System	Error	ω M05*	ω M05s*	ω M05*	ω M05s*	ω M05*	ω M05s*	ω M05*	ω M05s*
Atoms	MSE	-0.15	0.24	0.05	0.63	0.23	0.97	0.46	1.33
(18)	MAE	2.02	2.09	1.81	2.35	2.00	3.36	3.22	5.05
G3/99	MSE	0.06	0.09	0.05	0.03	-0.04	-0.12	-0.18	-0.27
(223)	MAE	1.77	1.79	1.66	1.76	1.78	2.02	2.10	2.35
IP	MSE	-0.58	-1.48	-0.84	-1.36	-0.38	-0.32	0.30	0.73
(40)	MAE	2.75	3.06	2.81	3.08	2.68	2.81	2.64	2.79
EA	MSE	-1.50	-1.70	-1.29	-1.15	-0.94	-0.70	-0.64	-0.39
(25)	MAE	2.50	2.56	2.33	2.22	2.07	1.97	1.98	1.91
PA	MSE	-1.65	-2.68	-1.49	-2.71	-1.07	-2.11	-0.78	-1.54
(8)	MAE	1.87	2.68	1.83	2.82	1.79	2.53	1.86	2.43
NHTBH	MSE	-1.26	-1.09	-0.68	-0.39	0.08	0.40	0.85	1.17
(38)	MAE	1.98	1.82	1.51	1.40	1.46	1.67	1.71	1.95
HTBH	MSE	-1.96	-1.95	-1.95	-1.68	-1.61	-1.24	-1.21	-0.84
(38)	MAE	2.19	2.08	2.12	1.84	1.95	1.56	1.86	1.47
S22	MSE	2.65	1.91	1.80	1.06	1.01	0.56	0.45	0.26
(22)	MAE	2.65	1.91	1.80	1.06	1.02	0.67	0.71	0.63
All	MSE	-0.31	-0.42	-0.30	-0.35	-0.21	-0.18	-0.11	-0.02
(412)	MAE	2.03	2.03	1.86	1.90	1.84	2.01	2.06	2.28

TABLE III. Statistical errors (in kcal/mol) of the training set. The M05-D* and M05* functionals are defined in the text. M05-2X was not particularly parametrized using this training set.

System	Error	ω M05-D	ω M05s-D	M05-D*	M05*	M05-2X	ω B97X-D
Atoms	MSE	0.37	0.83	0.18	-0.48	-3.01	-0.05
(18)	MAE	2.02	2.28	2.61	1.98	5.10	2.57
G3/99	MSE	-0.03	-0.03	-0.10	-0.05	2.01	-0.24
(223)	MAE	1.62	1.73	1.78	1.78	3.65	1.93
IP	MSE	-0.80	-1.33	0.06	0.27	1.10	0.19
(40)	MAE	2.86	3.04	2.84	2.51	3.35	2.74
EA	MSE	-1.02	-0.98	-0.54	-0.84	-0.23	0.07
(25)	MAE	2.12	2.13	2.13	2.35	2.48	1.91
PA	MSE	-1.48	-2.66	-0.94	-1.76	-1.26	1.42
(8)	MAE	2.10	3.07	1.31	2.17	1.51	1.50
NHTBH	MSE	-0.94	-0.59	-1.38	-1.32	0.13	-0.45
(38)	MAE	1.57	1.53	2.04	2.08	1.75	1.51
HTBH	MSE	-2.82	-2.33	-2.95	-1.77	-0.65	-2.57
(38)	MAE	2.83	2.37	3.08	2.14	1.51	2.70
S22	MSE	-0.01	-0.01	0.04	3.46	0.73	-0.08
(22)	MAE	0.27	0.21	0.23	3.46	0.87	0.21
All	MSE	-0.51	-0.49	-0.49	-0.21	1.02	-0.36
(412)	MAE	1.83	1.89	1.99	2.05	3.05	1.96

TABLE IV. Statistical errors (in kcal/mol) of the test sets.

System	Error	ω M05-D	ω M05s-D	M05-2X	ω B97X-D
G3/05	MSE	-0.85	-1.67	0.00	0.25
(48)	MAE	3.21	3.79	5.24	3.02
RE	MSE	-0.58	-0.65	-0.86	-0.24
(30)	MAE	1.49	1.32	1.65	1.63
Non-covalent	MSE	-0.11	-0.05	0.50	-0.15
(29)	MAE	0.31	0.30	0.61	0.43
All	MSE	-0.58	-0.95	-0.11	0.01
(107)	MAE	1.94	2.15	2.98	1.93

detailed information of the test sets as well as the basis sets, and numerical grids used is given in Ref. [35].

A. Atomization Energies, Reaction Energies, and Noncovalent Interactions

Table IV summarized the general energetic results in the same way as in Ref. [36], for convenience of further comparisons. Since the 30 chemical reaction energies are taken from the NHTBH38/04 and HTBH38/04 databases calculated in Table III, the EML(75,302) grid is used. In Table IV, the comparison between ω M05-D and ω M05s-D shows noticeable difference in atomization energies, and makes great influence on the choice of our proposed functional.

B. Equilibrium Geometries

Satisfactory predictions of molecular geometries of covalent and non-covalent systems by density functionals are necessary for practical use. For covalent systems, we perform geometry optimizations for each functional on the equilibrium experimental test set (EXTS) [73], while for non-covalent systems, we compute the intermolecular bond lengths of 12 weakly bound complexes taken from the S22 set [64], using 6-311++G(3df,3pd) basis set with the EML(75,302) grid. As shown in Table V, performance of all the hybrid functionals in predicting optimized geometries of EXTS is similar, while the performance of simple model (ω M05s-D) is somewhat worse for the

TABLE V. Statistical errors (in Å) of EXTS (Ref. [73]) and bond lengths of 12 weakly bound complexes from the S22 set (Ref. [64]). The results of ω B97X-D are taken from Ref. [36].

System	Error	ω M05-D	ω M05s-D	M05-2X	ω B97X-D
EXTS (166)	MSE	0.003	0.001	-0.004	-0.002
	MAE	0.010	0.009	0.009	0.009
	rms	0.019	0.014	0.014	0.013
	Max(−)	-0.081	-0.083	-0.082	-0.078
	Max(+)	0.177	0.067	0.054	0.055
Weak (12)	MSE	-0.041	-0.069	-0.021	-0.044
	MAE	0.061	0.078	0.062	0.064
	rms	0.083	0.102	0.080	0.085
	Max(−)	-0.189	-0.195	-0.165	-0.198
	Max(+)	0.043	0.029	0.140	0.056

intermolecular bond lengths. We decide our proposed model to be ω M05-D in this subsection. For brevity, the performance of ω M05s-D will not be shown for subsequent calculations.

C. Dissociation of Symmetric Radical Cations

Common semilocal functionals are generally accurate for systems near equilibrium. However, due to considerable self-interaction errors in semilocal functionals, spurious fractional charge dissociation occurs [32, 74, 75]. This situation becomes amplified for symmetric charged radicals X_2^+ , such as H_2^+ , He_2^+ , Ne_2^+ and Ar_2^+ . Gräfenstein and coworkers have obtained qualitatively correct result for these systems [76, 77] using self-interaction-corrected DFT proposed by Perdew and Zunger [78], and confirmed that the errors of standard DFT methods should be dominated by the SIEs.

We perform unrestricted calculations with the aug-cc-pVQZ basis set and a high-quality EML(250,590) grid. The DFT results are compared with results from HF theory, and the very accurate CCSD(T) theory [79, 80]. The HF method is exact in Fig. 1, and gives qualitatively correct results from Fig. 2 to Fig. 4. Although ω M05-D has the same amount of LR HF exchange as ω B97X-D, the larger fraction of SR HF exchange included in ω M05-D helps to reduce its remaining SIE. Therefore, the error of ω M05-D is smaller than that of ω B97X-D, especially for larger cations (e.g. Ne_2^+ and Ar_2^+). The global hybrid functional M05-2X exhibits the undesirable X_2^+ dissociation

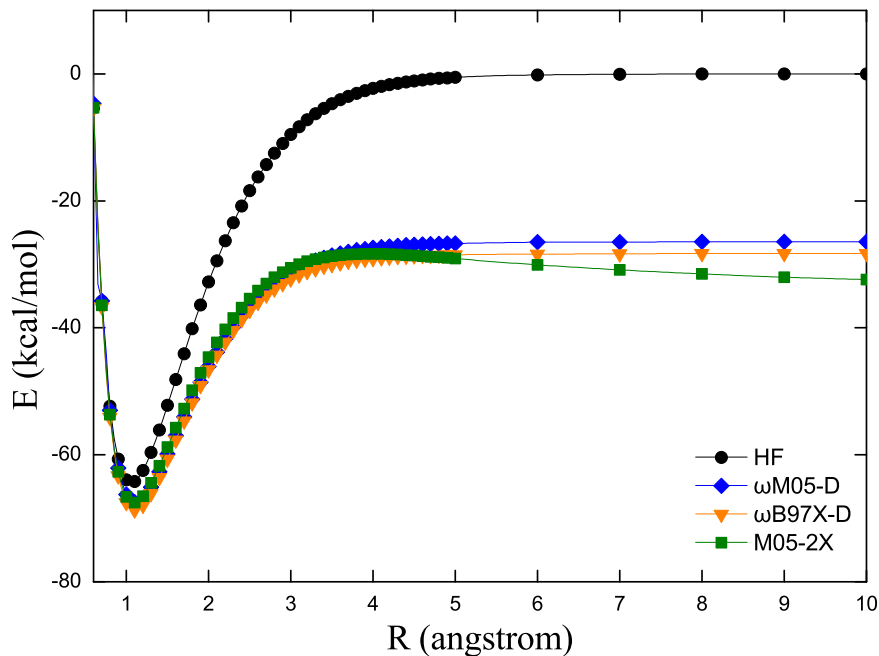


FIG. 1. Dissociation curve of H_2^+ . Zero level is set to $E(\text{H}) + E(\text{H}^+)$ for each method.

curves, displaying a spurious energy barrier at intermediate bond length R .

D. Frontier Orbital Energies

Let $\text{IP}(N)$ be the ionization potential and $\text{EA}(N)$ be the electron affinity of the N -electron system, which are defined as

$$\text{IP}(N) = E_{N-1} - E_N, \quad (39)$$

$$\text{EA}(N) = E_N - E_{N+1}, \quad (40)$$

respectively, with E_N being the total energy of N -electron system. For the exact DFT, the vertical ionization potential of a neutral molecule is identical to the minus HOMO (highest occupied molecular orbital) energy of the neutral molecule [3, 81],

$$\text{IP}(N) = -\epsilon_N(N), \quad (41)$$

and the vertical electron affinity of a neutral molecule is identical to the minus HOMO energy of the anion (since $\text{EA}(N) = \text{IP}(N + 1)$ by definition),

$$\text{EA}(N) = -\epsilon_{N+1}(N + 1), \quad (42)$$

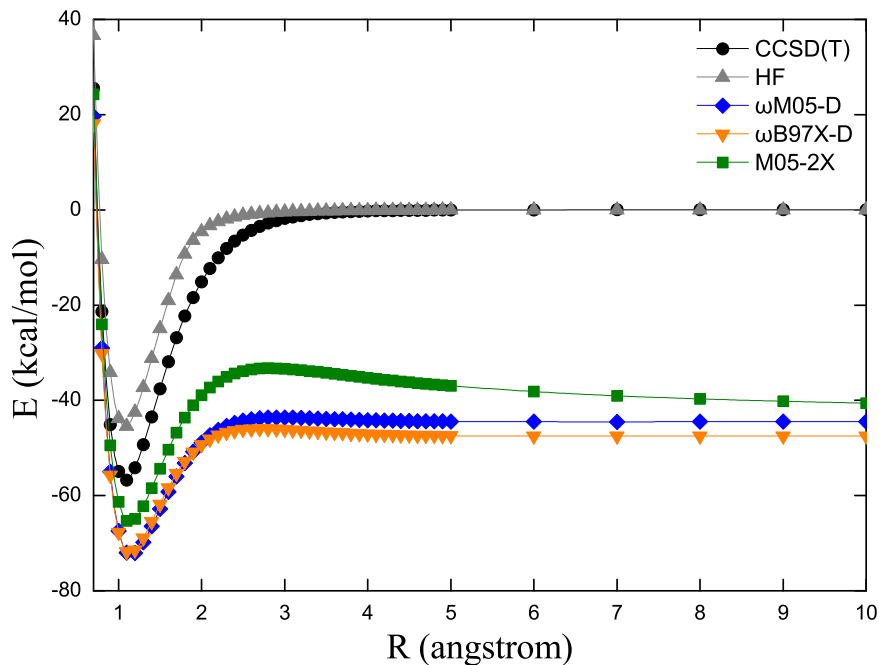


FIG. 2. Dissociation curve of He_2^+ . Zero level is set to $E(\text{He})+E(\text{He}^+)$ for each method.

where $\epsilon_M(N)$ is the M -th orbital energy of N -electron system. The vertical electron affinity of a neutral molecule may also be approximated by the minus LUMO (lowest unoccupied molecular orbital) energy of the neutral molecule, but it is proved that there exists a difference between the vertical EA and the minus LUMO energy,

$$\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N), \quad (43)$$

where the difference Δ_{xc} arises from the discontinuity of exchange-correlation potentials [82–84]. Recent study shows that Δ_{xc} is close to zero for LC hybrid functionals [85], so the minus LUMO energy calculated by a LC hybrid functional should be close to the vertical EA.

To evaluate the performance of the functionals on the HOMO energy of the neutral molecule, we collect a new database, IP131, which consists of experimental vertical IPs of 18 atoms and 113 molecules in the experimental geometries. The geometries and most of the reference values are collected from the NIST database [86]. Other publications [87] are adopted for the experimental vertical IPs of some molecules. The DFT calculations are performed with 6-311++G(3df,3pd) basis and EML(75,302) grid. As can be seen in Table VI, $\omega\text{M05-D}$ gives the best results. The global hybrid M05-2X gives the worst results here, due to its incorrect long-range XC-potential behavior.

To evaluate the performance of the functionals on the vertical electron affinity, we construct another database

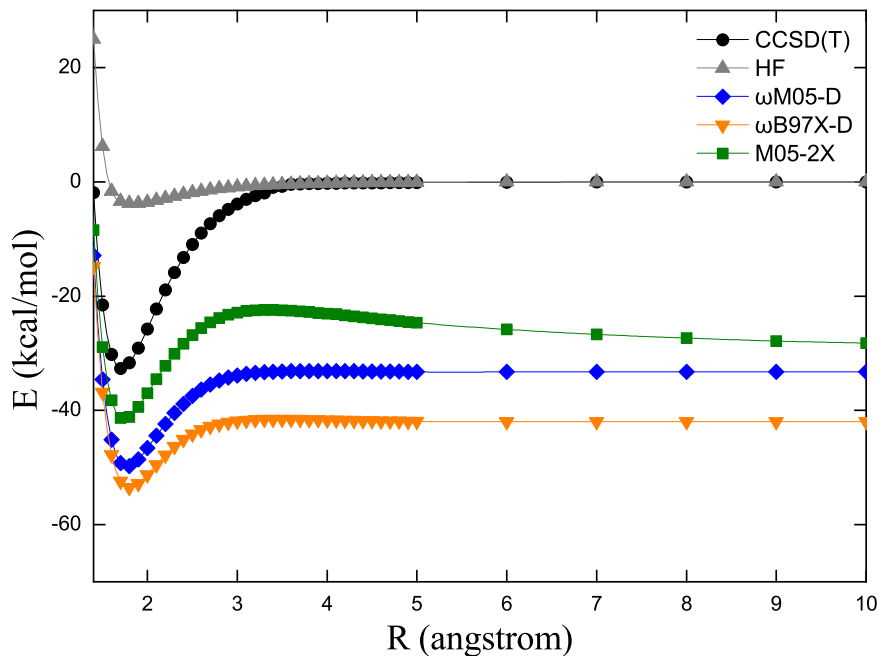


FIG. 3. Dissociation curve of Ne_2^+ . Zero level is set to $E(\text{Ne}) + E(\text{Ne}^+)$ for each method.

called EA115, which consists of 18 atoms and 97 molecules. For the molecular geometries, it is a subset of IP131. Because experimental vertical EAs are not as widely available as experimental vertical IPs, the reference values of vertical EAs are obtained via the accurate CCSD(T) calculations (using Eq. (40)). The CCSD(T) correlation energies in the basis-set limit are extrapolated from calculations using the aug-cc-pVTZ and aug-cc-pVQZ basis sets [88]:

$$E_{XY}^\infty = \frac{E_X^{\text{corr}} X^3 - E_Y^{\text{corr}} Y^3}{X^3 - Y^3}, \quad (44)$$

where $X=3$ and $Y=4$ for the aug-cc-pVTZ and aug-cc-pVQZ basis, respectively. The electron affinities are evaluated in two different ways, as shown in Table VII for the minus HOMO energy of the anion, and Table VIII for the minus LUMO energy of the neutral molecule. Clearly, the LC hybrid functionals outperform the global hybrid M05-2X. The reference values and molecular geometries of IP131 and EA115 are given in the supplementary material [71] along with detailed DFT results.

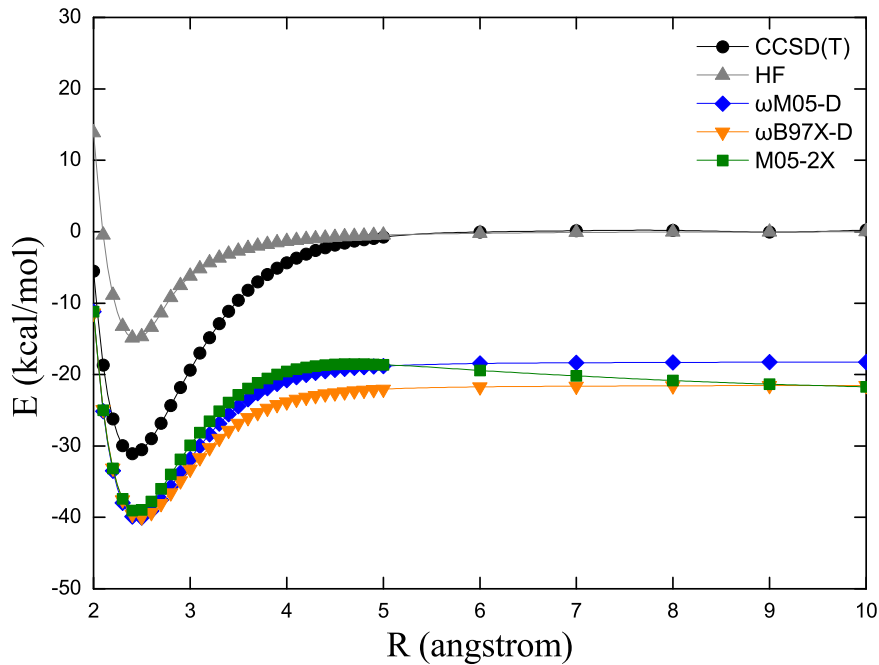


FIG. 4. Dissociation curve of Ar_2^+ . Zero level is set to $E(\text{Ar}) + E(\text{Ar}^+)$ for each method.

TABLE VI. Statistical errors (in eV) for the IP131 database. Error is defined as $-\epsilon_N(N) - \text{IP}_{\text{vertical}}$. Experimental geometries and reference values are used for all molecules.

System	Error	$\omega\text{M05-D}$	M05-2X	$\omega\text{B97X-D}$
atoms	MSE	-1.48	-2.06	-1.64
(18)	MAE	1.48	2.06	1.64
	rms	1.74	2.16	1.98
molecules	MSE	-0.68	-1.23	-0.92
(113)	MAE	0.68	1.23	0.92
	rms	0.76	1.27	1.00
total	MSE	-0.79	-1.34	-1.02
(131)	MAE	0.79	1.34	1.02
	rms	0.96	1.43	1.18

TABLE VII. Statistical errors (in eV) for the EA115 database. Error is defined as $-\epsilon_{N+1}(N+1) - \text{EA}_{\text{vertical}}$. Experimental geometries and CCSD(T) reference values are used for all molecules.

System	Error	ω M05-D	M05-2X	ω B97X-D
atoms	MSE	-0.46	-1.21	-0.53
(18)	MAE	0.49	1.21	0.57
	rms	0.73	1.35	0.84
moelcules	MSE	-0.54	-1.18	-0.54
(97)	MAE	0.55	1.18	0.56
	rms	0.80	1.32	0.82
total	MSE	-0.53	-1.18	-0.54
(115)	MAE	0.55	1.18	0.56
	rms	0.79	1.32	0.82

TABLE VIII. Statistical errors (in eV) of the minus LUMO energy of the neutral molecule for the EA115 database. Experimental geometries and CCSD(T) reference values are used for all molecules.

System	Error	ω M05-D	M05-2X	ω B97X-D
atoms	MSE	-0.27	0.57	-0.02
(18)	MAE	0.73	1.02	0.74
	rms	0.92	1.12	0.89
moelcules	MSE	-0.24	0.60	0.05
(97)	MAE	0.60	0.75	0.52
	rms	0.69	0.94	0.60
total	MSE	-0.24	0.60	0.04
(115)	MAE	0.62	0.79	0.55
	rms	0.73	0.97	0.65

E. Fundamental Gaps

The fundamental gap E_g of a molecule with N electrons is defined as

$$E_g = \text{IP}(N) - \text{EA}(N). \quad (45)$$

Following Eqs. (39) and (40) for the definitions of IP and EA, three self-consistent field (SCF) calculations (for the neutral molecule, cation and anion) are required to obtain the fundamental gap of a molecule. Using Eq. (41) and (42), the fundamental gap of a molecule can also be obtained by two SCF calculations (for the neutral molecule and anion).

Following Janak’s theorem [89], the fundamental gap can be approximated by the HOMO-LUMO gap [84]

$$\Delta_{KS} = \epsilon_{N+1}(N) - \epsilon_N(N), \quad (46)$$

and we can obtain the fundamental gap of a system using only one calculation. But from Eqs. (41), (42), (43), (45), and (46), we know that there exists a difference between the fundamental gap and HOMO-LUMO gap,

$$E_g = \Delta_{KS} + \Delta_{xc}. \quad (47)$$

As previously mentioned, Δ_{xc} has been shown to be close to zero for LC hybrid functionals [85], so the HOMO-LUMO gap calculated by a LC hybrid functional should be close to the fundamental gap.

To evaluate the performance of the functionals on fundamental gap, we construct another database called FG115, which shares the same molecular geometries with the EA115 database. For consistency, the reference values of fundamental gaps are also obtained via the CCSD(T) calculations described in the last subsection (using Eqs. (39), (40), and (45)).

To examine the performance of density functionals, we evaluate the fundamental gaps using three different estimates, with 6-311++G(3df,3pd) basis and EML(75,302) grid. The results are shown from Table IX to Table XI, in order of increasing the number of SCF calculations required for each molecule. In the estimate requiring three calculations, the results are similar for the three functionals. ω B97X-D gives worse results than other functionals in the estimate requiring two calculations. In the simplest estimate, the HOMO-LUMO gap, which requires only one SCF calculation for each system, ω M05-D significantly outperforms the other two functionals. The reference values of FG115 and detailed HOMO-LUMO gap results by DFT methods are given in the supplementary material [71].

F. Excitation Energies

To assess the performance of density functionals on excitation energies, we perform TDDFT calculations on five small molecules [90], which include nitrogen gas (N_2), carbon monoxide (CO), water (H_2O), ethylene (C_2H_4) and formaldehyde (CH_2O), with 6-311(2+,2+)G** basis and EML(99,590) grid. The molecular geometries, experimental values of excitation energy are taken from Ref. [90]. The detail results and mean absolute errors of all excited states are listed in Table XII. The new ω M05-D functional yields excellent performance, especially for the Rydberg

TABLE IX. Statistic errors (in eV) of HOMO-LUMO gaps for the FG115 database. The energy gap of each system is evaluated by only one SCF calculation.

System	Error	ω M05-D	M05-2X	ω B97X-D
atoms	MSE	-1.14	-2.56	-1.55
(18)	MAE	1.43	2.56	1.79
	rms	1.62	2.79	2.05
molecules	MSE	-0.62	-2.00	-1.15
(97)	MAE	0.73	2.00	1.15
	rms	0.93	2.13	1.34
total	MSE	-0.70	-2.08	-1.21
(115)	MAE	0.84	2.08	1.25
	rms	1.07	2.24	1.48

TABLE X. Statistic errors (in eV) of fundamental gaps for the FG115 database, each evaluated by the difference of HOMO energies between the neutral molecule and anion. The energy gap of each system is evaluated by two SCF calculations.

System	Error	ω M05-D	M05-2X	ω B97X-D
atoms	MSE	-0.95	-0.83	-1.04
(18)	MAE	0.98	0.87	1.08
	rms	1.17	1.00	1.30
molecules	MSE	-0.31	-0.42	-0.55
(97)	MAE	0.56	0.51	0.72
	rms	0.70	0.60	0.85
total	MSE	-0.41	-0.48	-0.63
(115)	MAE	0.62	0.57	0.78
	rms	0.79	0.68	0.93

excitations. Note that ω M05-D outperforms ω B97X-D in both HOMO energies and Rydberg excitations, due to the larger fraction of short-range HF exchange included in ω M05-D (both functionals possess the same amount of LR-HF exchange).

Following Dreuw *et al.*, we perform TDDFT calculations for the lowest charge-transfer (CT) excitation between ethylene and tetrafluoroethylene, with a separation of R . Dreuw *et al.* have shown that the exact CT excitation

TABLE XI. Statistic errors (in eV) of IP-EA values for the FG115 database. The energy gap of each system is evaluated by three SCF calculations.

System	Error	ω M05-D	M05-2X	ω B97X-D
atoms	MSE	0.28	0.33	0.28
(18)	MAE	0.35	0.36	0.36
	rms	0.60	0.63	0.59
molecules	MSE	0.34	0.42	0.22
(97)	MAE	0.44	0.50	0.39
	rms	0.73	0.78	0.68
total	MSE	0.33	0.40	0.23
(115)	MAE	0.43	0.48	0.39
	rms	0.71	0.75	0.66

energy from the HOMO of donor to the LUMO of acceptor should have the following asymptote [91]:

$$\omega_{\text{CT}}(R \rightarrow \infty) \approx -\frac{1}{R} + \text{IP}_{\text{D}} - \text{EA}_{\text{A}}, \quad (48)$$

where IP_{D} is the ionization potential of donor and EA_{A} is the electron affinity of acceptor. Fig. 5 shows the trend of the excitation curves, and indicates the LC hybrid functionals obviously outperforms the global hybrid M05-2X. For the values of the excitation energies, as shown in Fig. 6, ω M05-D is about 0.2 electron volt better than ω B97X-D.

VI. CONCLUSIONS

We have developed a LC hybrid MGGA-D functional, called ω M05-D, which includes 100% long-range exact exchange, a fraction ($\approx 37\%$) of short-range exact exchange, a modified M05 exchange density functional for short-range interaction, the M05 correlation density functional [18, 19], and empirical atomic-pairwise dispersion corrections. For the modified short-range M05 exchange density functional, we have investigated two models. After comparisons in the training set and test sets, we decide to propose the one based on our new LC scheme ω M05-D, and marked the trial one as ω M05s-D. When the constraint of $\omega = 0$ is applied, ω M05-D and ω M05s-D are both reduced to the existing M05 functional form [18, 19] with the same empirical atomic-pairwise dispersion corrections. The constrained form ($\omega = 0$), when re-optimized on the same training set, provides worse performance on the training set, indicating that the single extra degree of freedom corresponding to long-range exchange is of physical significance to a hybrid MGGA.

TABLE XII. Vertical excitation energies (in eV) of several low-lying excited states of N₂, CO, water, formaldehyde and ethylene using 6-311(2+,2+)G** basis set. The geometries and experimental values are taken from Ref. [90].

Mol.	State	Exp.	ω M05-D	M05-2X	ω B97X-D
N ₂	V ¹ Π_g	9.31	9.30	9.42	9.38
	V ¹ Σ_u^-	9.97	8.76	8.35	9.31
	V ¹ Δ_u	10.27	10.14	10.51	9.82
	V ³ Σ_u^+	7.75	7.86	8.30	7.17
	V ³ Π_g	8.04	7.94	8.12	7.82
	V ³ Δ_u	8.88	8.74	8.35	8.23
	V ³ Σ_u^-	9.67	8.76	9.26	9.31
	V ³ Π_u	11.19	11.30	11.72	10.98
CO	V ¹ Π	8.51	8.51	8.74	8.47
	V ¹ Σ^-	9.88	9.36	9.11	9.78
	V ³ Π	6.32	6.66	7.03	6.07
	V ³ Σ^+	8.51	8.47	8.87	8.00
	V ³ Δ	9.36	9.19	9.11	8.88
	V ³ Σ^-	9.88	9.36	9.55	9.78
H ₂ O	R ¹ B ₁	7.4	7.68	8.04	7.23
	R ¹ A ₂	9.1	9.14	9.60	8.63
	R ¹ A ₁	9.7	9.73	10.29	9.20
	R ¹ B ₁	10.0	9.72	10.32	9.17
	R ¹ A ₁	10.17	10.06	10.71	9.49
	R ³ B ₁	7.2	7.27	7.66	6.89
C ₂ H ₄	R ¹ B _{3u}	7.11	7.53	7.61	7.02
	V ¹ B _{1u}	7.60	7.80	8.07	7.52
	R ¹ B _{1g}	7.80	7.87	8.07	7.59
	R ¹ B _{2g}	8.01	8.15	8.19	7.66
	R ¹ A _g	8.29	8.36	8.52	7.87
	R ¹ B _{3u}	8.62	8.76	8.80	8.36
	V ³ B _{1u}	4.36	4.64	4.99	4.12
	R ³ B _{3u}	6.98	7.43	7.48	6.92
	R ³ B _{1g}	7.79	7.47	7.82	7.50
	R ³ B _{2g}	7.79	8.06	8.07	7.56
	R ³ A _g	8.15	8.12	8.11	7.63
CH ₂ O	V ¹ A ₂	4.07	3.63	3.68	3.88
	R ¹ B ₂	7.11	7.48	7.92	6.96
	R ¹ B ₂	7.97	8.13	8.58	7.66
	R ¹ A ₁	8.14	9.13	9.47	8.74
	R ¹ A ₂	8.37	8.30	8.84	7.84
	R ¹ B ₂	8.88	8.86	9.21	8.52
	V ³ A ₂	3.50	3.02	3.12	3.21
	V ³ A ₁	5.86	5.70	6.02	5.29
	R ³ B ₂	6.83	7.33	7.74	6.81
	R ³ B ₂	7.79	7.97	8.37	7.50
	R ³ A ₁	7.96	8.06	8.45	7.56
MAE	Valence		0.31	0.46	0.32
	Rydberg		0.22	0.47	0.35

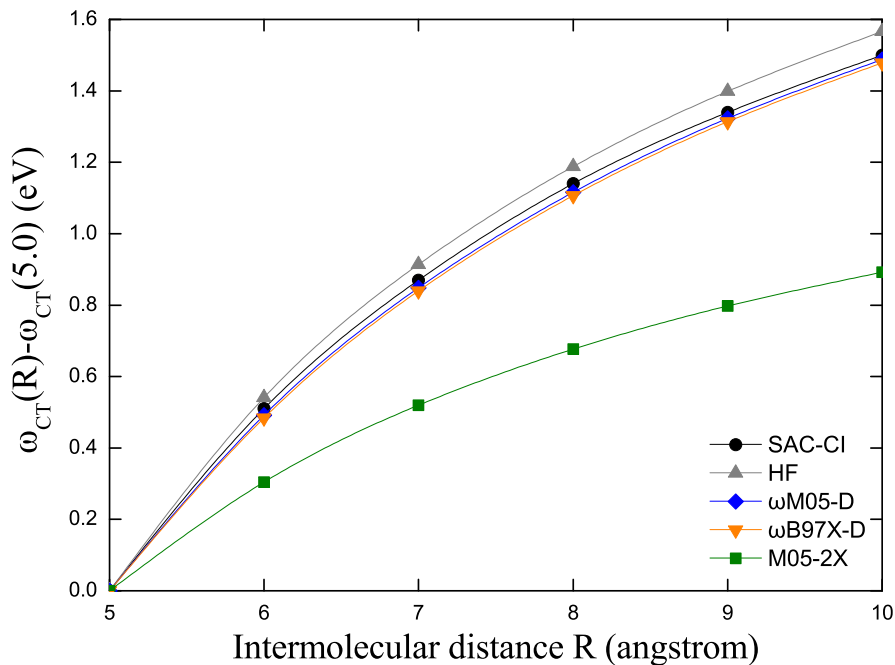


FIG. 5. The lowest CT excitation of $\text{C}_2\text{H}_4 \cdots \text{C}_2\text{F}_4$ dimer along the intermolecular distance R (in Å). For all functionals, the excitation at 5 Å is set to zero.

Since $\omega\text{M05-D}$ is a parametrized functional, we test it against the trial simple model $\omega\text{M05s-D}$ as well as two closely related functionals (M05-2X [19] and $\omega\text{B97X-D}$ [36]) on a separate independent test set of data, which includes further atomization energies, reaction energies, noncovalent interaction energies, equilibrium geometries, energy curve for homonuclear diatomic cation dissociations, frontier orbital energies and fundamental gaps. The three databases assessing frontier orbital energies and fundamental gaps are presented for the first time. For excitation energies, we calculate valence and Rydberg excitations, as well as a charge-transfer excited state. Compared to $\omega\text{M05s-D}$, noticeable difference in transferability for atomization energies largely decides our proposed model. $\omega\text{M05-D}$ consistently outperforms M05-2X (and performs comparably to $\omega\text{B97X-D}$) on the test sets, and shows smaller SIE and better asymptotic behavior relative to both the M05-2X and $\omega\text{B97X-D}$.

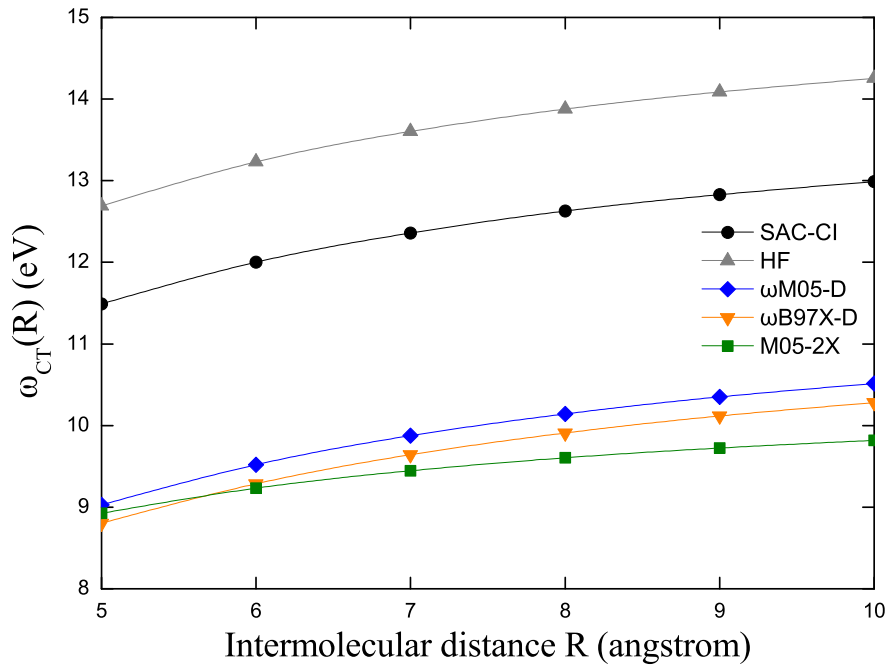


FIG. 6. The lowest CT excitation of $C_2H_4 \cdots C_2F_4$ dimer along the intermolecular distance R (in Å).

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SUPPLEMENTARY MATERIAL

TABLE XIII: $-\epsilon_N(N)$ (in eV) of IP131 database. Most experimental reference values are collected from the NIST database, [86] while other publications [87] are adopted for the molecules marked.

Molecule	Reference	ω M05-D	M05-2X	ω B97X-D
H (Hydrogen atom)	13.60	11.10	10.44	11.04
He (Helium atom)	24.59	20.75	20.75	20.18
Li (Lithium atom)	5.39	5.06	4.19	5.22
Be (Beryllium atom) [87]	9.32	8.19	7.29	8.27
B (Boron atom)	8.30	7.21	6.39	7.24
C (Carbon atom)	11.26	9.74	9.11	9.57
N (Nitrogen atom)	14.53	12.46	12.02	12.13
O (Oxygen atom)	13.62	11.80	11.51	11.48
F (Fluorine atom)	17.42	15.15	15.10	14.63
Ne (Neon atom)	21.57	18.77	18.93	18.06
Na (Sodium atom)	5.14	4.92	4.08	4.87
Mg (Magnesium atom)	7.65	7.15	6.36	7.07
Al (Aluminum atom)	5.99	5.33	4.43	5.47
Si (Silicon atom)	8.15	7.29	6.42	7.29
P (Phosphorus atom)	10.49	9.33	8.51	9.25
S (Sulfur atom)	10.36	9.33	8.65	9.30
Cl (Chlorine atom)	12.97	11.70	11.12	11.56
Ar (Argon atom)	15.76	14.17	13.68	13.93
CH ₃ (Methyl radical)	9.84	8.79	7.92	8.60
CH ₄ (Methane)	13.60	13.16	12.59	12.97
NH (Imidogen) ($^3\Sigma^-$)	13.49	11.97	11.51	11.64
NH ₂ (Amino radical)	12.00	10.99	10.47	10.74
NH ₃ (Ammonia)	10.82	10.01	9.41	9.74
OH (Hydroxyl radical)	13.02	11.64	11.32	11.26

H ₂ O (Water) [87]	12.62	11.51	11.10	11.10
HF (Hydrogen fluoride)	16.12	14.42	14.28	13.90
SiH ₃ (Silyl)	8.74	8.19	7.32	8.16
SiH ₄ (Silane)	12.30	11.86	11.18	11.80
PH ₃ (Phosphine)	10.59	9.79	9.03	9.76
H ₂ S (Hydrogen sulfide)	10.50	9.57	8.84	9.47
HCl (Hydrogen chloride) [87]	12.77	11.64	11.02	11.45
C ₂ H ₂ (Acetylene)	11.49	10.61	9.85	10.36
C ₂ H ₄ (Ethylene)	10.68	10.01	9.17	9.74
C ₂ H ₆ (Ethane)	11.99	11.70	11.15	11.59
HCN (Hydrogen cyanide)	13.61	12.62	11.97	12.35
CO (Carbon monoxide)	14.01	12.97	12.51	12.81
HCO (Formyl radical)	9.31	8.81	8.30	8.62
H ₂ CO (Formaldehyde)	10.89	10.09	9.60	9.82
CH ₃ OH (Methyl alcohol)	10.96	10.23	9.76	9.93
N ₂ (Nitrogen diatomic)	15.58	14.58	14.25	14.28
N ₂ H ₄ (Hydrazine)	8.98	9.03	8.46	8.79
NO (Nitric oxide)	9.26	8.70	8.35	8.35
O ₂ (Oxygen diatomic) (³ Σ _g)	12.30	11.48	11.26	11.02
H ₂ O ₂ (Hydrogen peroxide)	11.70	10.77	10.42	10.36
F ₂ (Fluorine diatomic)	15.70	14.44	14.39	13.90
CO ₂ (Carbon dioxide)	13.78	12.97	12.54	12.65
P ₂ (Phosphorus diatomic)	10.62	9.93	9.14	9.90
S ₂ (Sulfur diatomic) (³ Σ _g)	9.55	8.95	8.30	8.87
Cl ₂ (Chlorine diatomic)	11.49	10.77	10.17	10.64
NaCl (Sodium Chloride)	9.80	8.60	7.94	8.40
SiO (Silicon monoxide) [87]	11.61	10.88	10.20	10.77
CS (Carbon monosulfide) [87]	11.34	10.99	10.42	10.91
ClO (Monochlorine monoxide)	11.01	10.12	9.71	9.90
ClF (Chlorine monofluoride)	12.77	11.67	11.18	11.45
Si ₂ H ₆ (Disilane)	10.53	10.15	9.41	10.12

CH ₃ Cl (Methyl chloride)	11.29	10.61	9.98	10.42
CH ₃ SH (Methanethiol)	9.44	8.79	8.05	8.68
SO ₂ (Sulfur dioxide)	12.50	11.78	11.29	11.59
BF ₃ (Borane, trifluoro-)	15.96	14.82	14.72	14.28
BCl ₃ (Borane, trichloro-)	11.64	11.18	10.58	11.02
AlCl ₃ (Aluminum trichloride)	12.01	11.48	10.85	11.29
CF ₄ (Carbon tetrafluoride)	16.20	15.23	15.15	14.69
CCl ₄ (Carbon tetrachloride)	11.69	11.15	10.58	10.99
OCS (Carbonyl sulfide)	11.19	10.64	9.96	10.53
CS ₂ (Carbon disulfide)	10.09	9.57	8.89	9.57
CF ₂ O (Carbonic difluoride)	13.60	12.78	12.43	12.38
SiF ₄ (Silicon tetrafluoride)	16.40	15.37	15.26	14.85
N ₂ O (Nitrous oxide)	12.89	12.00	11.51	11.75
NF ₃ (Nitrogen trifluoride)	13.60	12.62	12.35	12.32
PF ₃ (Phosphorus trifluoride)	12.20	10.74	10.17	10.69
O ₃ (Ozone)	12.73	12.35	11.91	11.97
F ₂ O (Difluorine monoxide)	13.26	12.51	12.40	12.02
ClF ₃ (Chlorine trifluoride)	13.05	12.19	11.86	11.86
C ₂ F ₄ (Tetrafluoroethylene)	10.69	9.93	9.41	9.71
CF ₃ CN (Acetonitrile, trifluoro-)	14.30	13.30	12.73	13.00
CH ₃ CCH (Propyne)	10.37	9.82	9.08	9.60
CH ₂ CCH ₂ (Allene)	10.20	9.79	9.06	9.60
C ₃ H ₄ (Cyclopropene)	9.86	9.33	8.60	9.11
C ₃ H ₆ (Cyclopropane)	10.54	10.47	9.74	10.28
C ₃ H ₈ (Propane)	11.51	11.21	10.66	11.10
CH ₃ CCCH ₃ (2-Butyne)	9.79	9.19	8.46	8.98
C ₄ H ₆ (Cyclobutene)	9.43	9.19	8.43	8.98
CH ₃ CH(CH ₃)CH ₃ (Isobutane)	11.13	10.99	10.42	10.85
C ₆ H ₆ (Benzene)	9.25	9.28	8.49	9.06
CH ₂ F ₂ (Methane, difluoro-)	13.27	12.27	11.97	11.97
CHF ₃ (Methane, trifluoro-)	15.50	13.52	13.27	13.22

CH_2Cl_2 (Methylene chloride)	11.40	10.85	10.28	10.72
CHCl_3 (Chloroform)	11.50	10.85	10.28	10.72
CH_3NO_2 (Methane, nitro-)	11.29	11.12	10.77	10.72
CH_3SiH_3 (Methyl silane)	11.60	11.23	10.50	11.12
HCOOH (Formic acid)	11.50	10.69	10.23	10.36
CH_3CONH_2 (Acetamide)	10.00	9.66	9.17	9.36
$\text{C}_2\text{H}_5\text{N}$ (Aziridine)	9.85	9.36	8.73	9.11
C_2N_2 (Cyanogen)	13.51	12.78	12.19	12.54
CH_3NHCH_3 (Dimethylamine)	8.95	8.60	7.97	8.38
CH_2CO (Ketene)	9.64	9.19	8.49	9.00
$\text{C}_2\text{H}_4\text{O}$ (Ethylene oxide)	10.57	10.25	9.79	9.90
$\text{C}_2\text{H}_2\text{O}_2$ (Ethanedial)	10.60	10.12	9.63	9.87
$\text{CH}_3\text{CH}_2\text{OH}$ (Ethanol)	10.64	10.09	9.63	9.79
CH_3OCH_3 (Dimethyl ether)	10.10	9.66	9.14	9.36
$\text{C}_2\text{H}_4\text{S}$ (Thiirane)	9.05	8.57	7.86	8.46
CH_3SOCH_3 (Dimethyl sulfoxide)	9.10	8.76	8.16	8.57
CH_2CHF (Ethene, fluoro-)	10.63	9.90	9.17	9.66
$\text{CH}_3\text{CH}_2\text{Cl}$ (Ethyl chloride)	11.06	10.44	9.85	10.28
CH_2CHCl (Ethene, chloro-)	10.20	9.60	8.87	9.41
CH_3COCl (Acetyl Chloride)	11.03	10.77	10.23	10.53
$\text{CH}_2\text{ClCH}_2\text{CH}_3$ (Propane, 1-chloro-)	10.88	10.42	9.76	10.25
$\text{N}(\text{CH}_3)_3$ (Trimethylamine)	8.54	8.27	7.62	8.05
$\text{C}_4\text{H}_4\text{O}$ (Furan)	8.90	8.70	7.92	8.51
$\text{C}_4\text{H}_5\text{N}$ (Pyrrole)	8.23	8.13	7.32	7.92
NO_2 (Nitrogen dioxide)	11.23	10.72	10.42	10.36
SF_6 (Sulfur Hexafluoride) [87]	15.70	14.96	14.91	14.42
CFCl_3 (Trichloromonofluoromethane)	11.76	11.23	10.66	11.07
CF_3Cl (Methane, chlorotrifluoro-)	13.08	12.27	11.75	12.05
CF_3Br (Bromotrifluoromethane) [87]	12.08	11.29	10.74	11.12
HCCF (Fluoroacetylene) [87]	11.50	10.53	9.85	10.28
HCCCN (Cyanoacetylene) [87]	11.75	11.07	10.42	10.85

C ₄ N ₂ (2-Butynedinitrile) [87]	11.84	11.56	10.96	11.34
C ₂ N ₂ (Cyanogen)	13.51	12.78	12.19	12.54
C ₃ O ₂ (Carbon suboxide) [87]	10.80	10.39	9.82	10.23
FCN (Cyanogen fluoride) [87]	13.65	12.46	11.89	12.16
C ₄ H ₂ (Diacetylene)	10.30	9.71	9.00	9.52
H ₂ CS (Thioformaldehyde)	9.38	8.73	8.02	8.62
CHONH ₂ (Formamide) [87]	10.40	9.90	9.44	9.57
CH ₂ CHCHO (Acrolein) [87]	10.10	9.90	9.38	9.57
CH ₂ CCl ₂ (Ethene, 1,1-dichloro-)	10.00	9.57	8.87	9.41
C ₂ HF ₃ (Trifluoroethylene) [87]	10.62	9.74	9.14	9.52
CH ₂ CF ₂ (Ethene, 1,1-difluoro-) [87]	10.70	10.01	9.33	9.76
CH ₃ F (Methyl fluoride)	13.04	12.21	11.86	11.91
CF ₂ Cl ₂ (Difluorodichloromethane)	12.24	11.61	11.07	11.45
SiF ₂ (Silicon difluoride)	11.08	10.25	9.52	10.23
MSE		-0.79	-1.34	-1.02
MAE		0.79	1.34	1.02
rms		0.96	1.43	1.18

TABLE XIV: $-\epsilon_{N+1}(N+1)$ and $-\epsilon_{N+1}(N)$ (in eV) of EA115 database. Reference values are calculated by the CCSD(T) theory.

molecule	reference	ω M05-D		M05-2X		ω B97X-D	
		$-\epsilon_{N+1}(N+1)$	$-\epsilon_{N+1}(N)$	$-\epsilon_{N+1}(N+1)$	$-\epsilon_{N+1}(N)$	$-\epsilon_{N+1}(N+1)$	$-\epsilon_{N+1}(N)$
H (Hydrogen atom)	0.75	0.84	-0.52	-0.08	-0.53	0.84	-0.53
He (Helium atom)	-2.63	-4.35	-4.76	-5.17	-3.89	-4.27	-4.30
Li (Lithium atom)	0.62	0.68	-0.44	0.00	0.14	0.71	-0.19
Be (Beryllium atom)	-0.36	-0.46	-0.52	-1.20	0.35	-0.41	-0.30
B (Boron atom)	0.25	0.19	0.38	-0.65	1.28	0.16	0.57
C (Carbon atom)	1.25	0.87	1.69	0.08	2.42	0.73	1.99
N (Nitrogen atom)	-0.22	-0.60	0.49	-1.39	1.55	-0.63	0.52
O (Oxygen atom)	1.45	0.76	2.18	0.16	2.96	0.54	2.48

F (Fluorine atom)	3.44	2.28	4.30	1.90	4.81	1.93	4.90
Ne (Neon atom)	-5.31	-7.18	-7.07	-8.16	-5.82	-7.53	-6.83
Na (Sodium atom)	0.54	0.68	-0.49	0.05	-0.03	0.68	-0.24
Mg (Magnesium atom)	-0.23	-0.41	-0.65	-0.98	0.11	-0.30	-0.38
Al (Aluminum atom)	0.45	0.27	0.22	-0.54	1.12	0.33	0.35
Si (Silicon atom)	1.42	1.09	1.41	0.22	2.31	1.06	1.55
P (Phosphorus atom)	0.74	0.57	0.98	-0.24	2.20	0.63	1.20
S (Sulfur atom)	2.10	1.77	2.53	1.01	3.64	1.71	2.77
Cl (Chlorine atom)	3.69	3.05	4.27	2.34	5.22	2.91	4.57
Ar (Argon atom)	-2.81	-3.18	-3.78	-4.03	-2.53	-3.48	-3.40
CH ₃ (Methyl radical)	-0.07	-0.08	-0.08	-0.92	1.09	-0.16	-0.05
CH ₄ (Methane)	-0.62	-1.01	-1.52	-1.58	-0.92	-0.92	-1.17
NH (Imidogen)	0.33	-0.03	0.65	-0.79	1.66	-0.14	0.84
NH ₂ (Amino radical)	0.74	0.44	0.90	-0.33	1.85	0.27	1.12
NH ₃ (Ammonia)	-0.56	-0.98	-1.52	-1.63	-0.76	-0.90	-1.12
OH (Hydroxyl radical)	1.83	1.22	2.15	0.63	2.91	0.95	2.53
H ₂ O (Water)	-0.56	-1.03	-1.50	-1.80	-0.68	-0.95	-1.09
HF (Hydrogen fluoride)	-0.63	-1.14	-1.47	-1.85	-0.73	-1.01	-1.12
SiH ₃ (Silyl)	0.93	0.79	1.14	-0.03	2.53	0.82	1.31
SiH ₄ (Silane)	-1.11	-1.09	-1.69	-1.60	-0.95	-1.06	-1.28
PH ₃ (Phosphine)	-1.21	-0.90	-1.50	-1.44	-0.71	-0.90	-1.09
SH ₂ (Hydrogen sulfide)	-0.49	-1.85	-1.41	-2.39	-0.63	-1.69	-1.03
HCl (Hydrogen chloride)	-0.52	-0.92	-1.36	-1.63	-0.54	-0.84	-0.98
C ₂ H ₂ (Acetylene)	-1.90	-2.50	-1.52	-3.24	-1.09	-2.56	-1.22
C ₂ H ₄ (Ethylene)	-1.86	-2.07	-1.74	-2.86	-0.92	-2.12	-1.33
C ₂ H ₆ (Ethane)	-0.62	-1.03	-1.55	-1.55	-0.90	-0.95	-1.17
HCN (Hydrogen cyanide)	-0.48	-2.07	-1.41	-2.83	-0.92	-2.01	-1.09
CO (Carbon monoxide)	-1.50	-1.90	-1.33	-2.67	-0.46	-1.93	-1.09
HCO (Formyl radical)	0.02	-0.27	0.44	-1.01	1.39	-0.33	0.57
CH ₂ O (Formaldehyde)	-0.55	-1.31	-0.63	-2.09	0.19	-1.41	-0.46
CH ₃ OH (Methyl alcohol)	-0.55	-0.95	-1.44	-1.50	-0.79	-0.84	-1.09

N ₂ (Nitrogen diatomic)	-2.24	-2.80	-1.55	-3.56	-0.71	-2.88	-1.28
N ₂ H ₄ (Hydrazine)	-0.45	-1.52	-1.41	-1.99	-0.57	-1.39	-1.01
NO (Nitric oxide)	-0.42	-0.92	0.60	-1.52	1.44	-1.12	0.87
O ₂ (Oxygen diatomic)	-0.08	-0.87	0.79	-1.36	1.60	-1.09	1.12
H ₂ O ₂ (Hydrogen peroxide)	-0.92	-1.47	-1.63	-2.04	-0.82	-1.33	-1.25
F ₂ (Fluorine diatomic)	0.42	-0.38	1.69	-0.57	2.42	-0.73	2.15
CO ₂ (Carbon dioxide)	-0.65	-4.49	-1.69	-5.11	-0.73	-4.68	-1.31
P ₂ (Phosphorus diatomic)	0.48	0.33	0.73	-0.46	1.71	0.35	0.95
S ₂ (Sulfur diatomic)	1.53	1.12	1.69	0.44	2.72	1.12	1.93
Cl ₂ (Chlorine diatomic)	0.75	0.38	1.06	-0.33	1.99	0.27	1.33
NaCl (Sodium Chloride)	0.65	0.52	0.16	-0.16	0.79	0.65	0.46
SiO (Silicon monoxide)	0.03	-0.33	0.11	-1.12	1.09	-0.24	0.33
CS (Carbon monosulfide)	-0.09	-0.30	0.33	-1.03	1.25	-0.33	0.54
ClO (Monochlorine monoxide)	2.19	1.60	2.58	1.06	3.37	1.41	2.77
ClF (Chlorine monofluoride)	0.44	-0.14	0.92	-0.79	1.85	-0.22	1.28
Si ₂ H ₆ (Disilane)	-0.69	-1.22	-1.58	-1.69	-0.76	-1.17	-1.20
CH ₃ Cl (Methyl chloride)	-0.51	-0.84	-1.39	-1.47	-0.68	-0.76	-1.01
CH ₃ SH (Methanethiol)	-0.50	-0.87	-1.41	-1.44	-0.63	-0.79	-1.03
SO ₂ (Sulfur dioxide)	0.81	0.41	1.41	-0.19	2.42	0.30	1.66
BF ₃ (Borane, trifluoro-)	-1.04	-1.25	-1.71	-1.88	-0.82	-1.17	-1.31
BCl ₃ (Borane, trichloro-)	-0.17	-1.01	-0.16	-1.52	0.76	-0.98	-0.03
AlCl ₃ (Aluminum trichloride)	0.06	-0.08	-0.35	-0.79	0.73	-0.11	-0.19
CF ₄ (Carbon tetrafluoride)	-1.33	-1.96	-2.48	-2.53	-1.52	-1.82	-2.04
CCl ₄ (Carbon tetrachloride)	-0.46	-0.35	-0.41	-1.01	0.57	-0.35	-0.14
OCS (Carbonyl sulfide)	-0.74	-1.58	-1.03	-2.26	-0.08	-1.58	-0.82
CS ₂ (Carbon disulfide)	0.01	-0.11	0.16	-0.79	1.12	-0.11	0.35
CF ₂ O (Carbonic difluoride)	-2.37	-2.50	-1.55	-3.40	-0.65	-2.42	-1.36
SiF ₄ (Silicon tetrafluoride)	-0.81	-1.25	-1.66	-1.88	-0.63	-1.22	-1.22
N ₂ O (Nitrous oxide)	-2.01	-2.58	-1.58	-3.26	-0.65	-2.75	-1.36
NF ₃ (Nitrogen trifluoride)	-2.06	-2.88	-2.67	-3.64	-1.82	-2.86	-2.37
PF ₃ (Phosphorus trifluoride)	-1.23	-1.58	-1.88	-2.12	-0.98	-1.50	-1.55

O ₃ (Ozone)	1.93	1.90	3.24	1.58	4.22	1.55	3.48
F ₂ O (Difluorine monoxide)	-0.31	-1.01	0.44	-1.36	1.22	-1.17	0.82
ClF ₃ (Chlorine trifluoride)	1.20	0.63	1.60	0.14	2.56	0.52	1.90
C ₂ F ₄ (Tetrafluoroethylene)	-1.65	-2.42	-2.07	-2.94	-1.03	-2.34	-1.66
CH ₃ CCH (Propyne)	-1.13	-1.77	-1.41	-2.23	-0.82	-1.60	-1.06
CH ₂ CCH ₂ (Allene)	-0.56	-1.55	-1.60	-2.04	-0.92	-1.41	-1.22
C ₃ H ₄ (Cyclopropene)	-1.82	-2.01	-1.66	-2.80	-0.92	-2.07	-1.31
C ₃ H ₆ (Cyclopropane)	-0.65	-1.17	-1.71	-1.63	-1.03	-1.09	-1.33
CH ₂ F ₂ (Methane, difluoro-)	-0.58	-1.06	-1.52	-1.63	-0.95	-0.90	-1.20
CF ₃ H (Methane, trifluoro-)	-0.60	-1.17	-1.58	-1.85	-1.01	-1.01	-1.25
CH ₂ Cl ₂ (Methylene chloride)	-0.49	-0.82	-1.31	-1.50	-0.49	-0.73	-0.98
CHCl ₃ (Chloroform)	-0.83	-0.79	-1.01	-1.52	-0.05	-0.73	-0.76
CH ₃ NO ₂ (Methane, nitro-)	-0.37	-0.49	0.05	-1.06	0.98	-0.65	0.27
CH ₃ SiH ₃ (Methyl silane)	-0.53	-0.92	-1.47	-1.47	-0.73	-0.84	-1.09
HCOOH (Formic acid)	-0.57	-2.15	-1.63	-2.88	-0.87	-2.18	-1.25
CH ₃ CONH ₂ (Acetamide)	-0.31	-1.60	-1.22	-2.09	-0.49	-1.44	-0.84
C ₂ N ₂ (Cyanogen)	-0.19	-0.33	0.52	-1.03	1.47	-0.38	0.68
CH ₂ CO (Ketene)	-0.51	-1.41	-1.03	-1.96	-0.16	-1.28	-0.87
C ₂ H ₄ O (Ethylene oxide)	-0.86	-1.03	-1.60	-1.55	-0.95	-0.95	-1.22
C ₂ H ₂ O ₂ (Ethanedial)	0.69	0.63	1.28	-0.11	2.18	0.49	1.41
CH ₃ CH ₂ OH (Ethanol)	-0.53	-0.92	-1.44	-1.47	-0.76	-0.82	-1.09
CH ₃ OCH ₃ (Dimethyl ether)	-0.58	-1.01	-1.52	-1.47	-0.84	-0.90	-1.14
C ₂ H ₄ S (Thiirane)	-0.78	-1.25	-1.60	-1.69	-0.87	-1.14	-1.20
CH ₂ CHF (Ethene, fluoro-)	-0.88	-2.18	-1.66	-2.91	-1.01	-2.23	-1.28
CH ₃ CH ₂ Cl (Ethyl chloride)	-0.51	-0.90	-1.47	-1.44	-0.73	-0.79	-1.09
CH ₂ CHCl (Ethene, chloro-)	-1.11	-1.60	-1.41	-2.39	-0.52	-1.66	-1.20
CH ₃ CClO (Acetyl Chloride)	-0.85	-1.12	-0.79	-1.80	0.11	-1.14	-0.65
NO ₂ (Nitrogen dioxide)	1.44	0.90	1.99	0.38	3.02	0.76	2.18
CFCl ₃ (Trichloromonofluoromethane)	-0.68	-0.76	-0.65	-1.39	0.33	-0.73	-0.41
CF ₃ Cl (Methane, chlorotrifluoro-)	-1.06	-1.63	-1.82	-2.28	-0.84	-1.55	-1.52
HCCF (Fluoroacetylene)	-0.55	-0.95	-1.39	-1.47	-0.82	-0.82	-1.09

HCCCN (Cyanoacetylene)	-0.36	-0.76	-0.19	-1.52	0.71	-0.79	-0.08
C ₄ N ₂ (2-Butynedinitrile)	0.68	0.76	1.25	0.05	2.20	0.71	1.36
C ₂ N ₂ (Cyanogen)	-0.19	-0.33	0.52	-1.03	1.47	-0.38	0.68
C ₃ O ₂ (Carbon suboxide)	-0.74	-1.01	-0.19	-1.66	0.76	-1.12	-0.05
FCN (Cyanogen fluoride)	-0.66	-4.08	-1.31	-4.81	-0.33	-4.22	-0.95
C ₄ N ₂ (Diacetylene)	-0.64	-1.28	-0.92	-2.01	-0.03	-1.28	-0.82
H ₂ CS (Thioformaldehyde)	0.28	0.11	0.68	-0.68	1.55	0.05	0.82
CHONH ₂ (Formamide)	-0.35	-2.48	-1.33	-3.21	-0.63	-2.45	-0.95
CH ₂ CCl ₂ (Ethene, 1,1-dichloro-)	-1.07	-1.01	-1.12	-1.58	-0.19	-0.90	-0.98
C ₂ HF ₃ (Trifluoroethylene)	-0.54	-1.14	-1.60	-1.74	-0.92	-0.98	-1.25
CH ₂ CF ₂ (Ethene, 1,1-difluoro-)	-1.03	-2.26	-1.66	-2.96	-0.95	-2.31	-1.28
CH ₃ F (Methyl fluoride)	-0.58	-0.98	-1.50	-1.55	-0.90	-0.87	-1.14
CF ₂ Cl ₂ (Difluorodichloromethane)	-0.90	-1.31	-1.20	-1.90	-0.22	-1.28	-0.92
SiF ₂ (Silicon difluoride)	0.10	-0.27	0.22	-1.06	1.20	-0.19	0.44
MSE		-0.53	-0.24	-1.18	0.60	-0.54	0.04
MAE		0.55	0.62	1.18	0.79	0.56	0.55
rms		0.79	0.73	1.32	0.97	0.82	0.65

TABLE XV: Reference values of FG115 database calculated by the CCSD(T) theory, compared with HOMO-LUMO gap results by DFT methods.

Molecule	Reference	ω M05-D	M05-2X	ω B97X-D
H (Hydrogen atom)	12.86	11.62	10.98	11.57
He (Helium atom)	27.23	25.57	24.70	24.56
Li (Lithium atom)	4.22	5.49	4.05	5.41
Be (Beryllium atom)	9.66	8.70	6.94	8.57
B (Boron atom)	7.99	6.83	5.11	6.66
C (Carbon atom)	9.97	8.05	6.69	7.59
N (Nitrogen atom)	14.74	11.97	10.47	11.61
O (Oxygen atom)	12.14	9.63	8.54	9.00
F (Fluorine atom)	13.98	10.88	10.28	9.74

Ne (Neon atom)	26.91	25.84	24.75	24.89
Na (Sodium atom)	4.14	5.41	4.11	5.11
Mg (Magnesium atom)	7.76	7.81	6.26	7.45
Al (Aluminum atom)	5.53	5.11	3.32	5.11
Si (Silicon atom)	6.73	5.88	4.11	5.74
P (Phosphorus atom)	9.78	8.35	6.31	8.05
S (Sulfur atom)	8.23	6.80	5.00	6.53
Cl (Chlorine atom)	9.30	7.43	5.90	6.99
Ar (Argon atom)	18.65	17.95	16.21	17.33
CH ₃ (Methyl radical)	9.86	8.87	6.83	8.54
CH ₄ (Methane)	15.06	14.69	13.52	14.14
NH (Imidogen) ($^3\Sigma^-$)	13.17	11.32	9.85	10.80
NH ₂ (Amino radical)	11.34	10.09	8.62	9.63
NH ₃ (Ammonia)	11.54	11.53	10.17	10.85
OH (Hydroxyl radical)	11.27	9.49	8.40	8.73
H ₂ O (Water)	13.35	13.00	11.78	12.19
HF (Hydrogen fluoride)	16.91	15.88	15.01	15.01
SiH ₃ (Silyl)	7.95	7.04	4.79	6.85
SiH ₄ (Silane)	14.03	13.55	12.13	13.08
PH ₃ (Phosphine)	11.82	11.29	9.74	10.85
H ₂ S (Hydrogen sulfide)	11.00	10.99	9.47	10.50
HCl (Hydrogen chloride)	13.36	13.00	11.56	12.43
C ₂ H ₂ (Acetylene)	13.43	12.13	10.93	11.59
C ₂ H ₄ (Ethylene)	12.57	11.75	10.09	11.07
C ₂ H ₆ (Ethane)	13.41	13.25	12.05	12.76
HCN (Hydrogen cyanide)	14.31	14.04	12.89	13.44
CO (Carbon monoxide)	15.57	14.31	12.97	13.90
HCO (Formyl radical)	9.56	8.38	6.91	8.05
CH ₂ O (Formaldehyde)	11.56	10.72	9.41	10.28
CH ₃ OH (Methyl alcohol)	11.67	11.67	10.55	11.02
N ₂ (Nitrogen diatomic)	17.88	16.13	14.96	15.56

N ₂ H ₄ (Hydrazine)	10.29	10.44	9.03	9.79
NO (Nitric oxide)	10.11	8.11	6.91	7.48
O ₂ (Oxygen diatomic) (³ Σ _g)	12.52	10.69	9.66	9.90
H ₂ O ₂ (Hydrogen peroxide)	12.65	12.40	11.23	11.61
F ₂ (Fluorine diatomic)	15.53	12.76	11.97	11.75
CO ₂ (Carbon dioxide)	14.58	14.66	13.27	13.95
P ₂ (Phosphorus diatomic)	10.19	9.19	7.43	8.95
S ₂ (Sulfur diatomic) (³ Σ _g)	7.96	7.26	5.58	6.94
Cl ₂ (Chlorine diatomic)	10.93	9.71	8.19	9.30
NaCl (Sodium Chloride)	8.64	8.43	7.15	7.94
SiO (Silicon monoxide)	11.60	10.77	9.11	10.44
CS (Carbon monosulfide)	11.58	10.66	9.17	10.36
ClO (Monochlorine monoxide)	8.85	7.53	6.34	7.13
ClF (Chlorine monofluoride)	12.43	10.74	9.33	10.17
Si ₂ H ₆ (Disilane)	11.33	11.72	10.17	11.32
CH ₃ Cl (Methyl chloride)	12.01	12.00	10.66	11.42
CH ₃ SH (Methanethiol)	10.01	10.20	8.68	9.71
SO ₂ (Sulfur dioxide)	11.74	10.36	8.87	9.93
BF ₃ (Borane, trifluoro-)	17.22	16.54	15.53	15.59
BCl ₃ (Borane, trichloro-)	12.07	11.34	9.82	11.04
AlCl ₃ (Aluminum trichloride)	12.13	11.83	10.12	11.48
CF ₄ (Carbon tetrafluoride)	17.85	17.71	16.67	16.73
CCl ₄ (Carbon tetrachloride)	11.97	11.56	10.01	11.12
OCS (Carbonyl sulfide)	12.13	11.67	10.04	11.34
CS ₂ (Carbon disulfide)	10.19	9.41	7.78	9.22
CF ₂ O (Carbonic difluoride)	16.08	14.33	13.08	13.74
SiF ₄ (Silicon tetrafluoride)	16.95	17.03	15.88	16.08
N ₂ O (Nitrous oxide)	15.01	13.57	12.16	13.11
NF ₃ (Nitrogen trifluoride)	15.76	15.29	14.17	14.69
PF ₃ (Phosphorus trifluoride)	13.00	12.62	11.15	12.24
O ₃ (Ozone)	11.06	9.11	7.70	8.49

F_2O (Difluorine monoxide)	13.82	12.08	11.18	11.21
ClF_3 (Chlorine trifluoride)	11.79	10.58	9.30	9.96
C_2F_4 (Tetrafluoroethylene)	12.45	12.00	10.44	11.37
CH_3CCH (Propyne)	11.69	11.23	9.90	10.66
CH_2CCH_2 (Allene)	10.83	11.40	9.98	10.83
C_3H_4 (Cyclopropene)	11.87	10.99	9.52	10.42
C_3H_6 (Cyclopropane)	11.64	12.19	10.77	11.61
CH_2F_2 (Methane, difluoro-)	14.15	13.79	12.92	13.16
CF_3H (Methane, trifluoro-)	15.44	15.10	14.28	14.47
CH_2Cl_2 (Methylene chloride)	12.18	12.16	10.77	11.70
CHCl_3 (Chloroform)	12.38	11.86	10.34	11.48
CH_3NO_2 (Methane, nitro-)	11.94	11.07	9.79	10.44
CH_3SiH_3 (Methyl silane)	12.35	12.70	11.23	12.21
HCOOH (Formic acid)	11.98	12.32	11.10	11.61
CH_3CONH_2 (Acetamide)	10.05	10.88	9.66	10.20
C_2N_2 (Cyanogen)	13.90	12.27	10.72	11.86
CH_2CO (Ketene)	10.32	10.23	8.65	9.87
$\text{C}_2\text{H}_4\text{O}$ (Ethylene oxide)	11.68	11.86	10.74	11.12
$\text{C}_2\text{H}_2\text{O}_2$ (Ethanedial)	10.04	8.84	7.45	8.46
$\text{CH}_3\text{CH}_2\text{OH}$ (Ethanol)	11.38	11.53	10.39	10.88
CH_3OCH_3 (Dimethyl ether)	10.79	11.18	9.98	10.50
$\text{C}_2\text{H}_4\text{S}$ (Thiirane)	9.93	10.17	8.73	9.66
CH_2CHF (Ethene, fluoro-)	11.55	11.56	10.17	10.93
$\text{CH}_3\text{CH}_2\text{Cl}$ (Ethyl chloride)	11.74	11.91	10.58	11.37
CH_2CHCl (Ethene, chloro-)	11.35	11.02	9.38	10.61
CH_3COCl (Acetyl Chloride)	11.97	11.56	10.12	11.18
NO_2 (Nitrogen dioxide)	9.79	8.73	7.40	8.19
CFCl_3 (Trichloromonofluoromethane)	12.61	11.89	10.34	11.48
CF_3Cl (Methane, chlorotrifluoro-)	14.27	14.09	12.59	13.57
HCCF (Fluoroacetylene)	12.04	11.91	10.66	11.37
HCCCN (Cyanoacetylene)	12.20	11.26	9.71	10.93

C_4N_2 (2-Butynedinitrile)	11.52	10.31	8.76	9.98
C_2N_2 (Cyanogen)	13.90	12.27	10.72	11.86
C_3O_2 (Carbon suboxide)	11.64	10.58	9.06	10.28
FCN (Cyanogen fluoride)	14.33	13.76	12.21	13.11
C_4H_2 (Diacetylene)	11.00	10.64	9.03	10.34
H_2CS (Thioformaldehyde)	9.18	8.05	6.47	7.81
$CHONH_2$ (Formamide)	10.81	11.23	10.06	10.53
CH_2CCl_2 (Ethene, 1,1-dichloro-)	11.17	10.69	9.06	10.39
C_2HF_3 (Trifluoroethylene)	11.11	11.34	10.06	10.77
CH_2CF_2 (Ethene, 1,1-difluoro-)	11.81	11.67	10.28	11.04
CH_3F (Methyl fluoride)	14.09	13.71	12.76	13.06
CF_2Cl_2 (Difluorodichloromethane)	13.33	12.81	11.29	12.38
SiF_2 (Silicon difluoride)	11.04	10.04	8.32	9.79
MSE		-0.70	-2.08	-1.21
MAE		0.84	2.08	1.25
rms		1.07	2.24	1.48

TABLE XVI: Experimental molecular geometries (in angstrom) for IP131, EA115 and FG115 databases collected from the NIST database [86]. The integers following the molecule are in order the spin multiplicities of neutral species, cation and anion. The molecules with only the spin multiplicity of the neutral species shown are in neither EA115 nor FG115 database. The spin multiplicities of neutral species are experimental values specified in the NIST database [86]. Each spin multiplicity of cations and anions is decided by CCSD(T)/aug-cc-pVTZ calculations, and corresponds to the lowest energy in between various spin multiplicities.

H (Hydrogen atom)	2	Null	1
H			
He (Helium atom)	1	2	2
He			
Li (Lithium atom)	2	1	1
Li			
Be (Beryllium atom)	1	2	2
Be			
B (Boron atom)	2	1	3
B			
C (Carbon atom)	3	2	4
C			
N (Nitrogen atom)	4	3	3
N			
O (Oxygen atom)	3	4	2
O			
F (Fluorine atom)	2	3	1
F			
Ne (Neon atom)	1	2	2
Ne			

Na (Sodium atom) 2 1 1

Na

Mg (Magnesium atom) 1 2 2

Mg

Al (Aluminum atom) 2 1 3

Al

Si (Silicon atom) 3 2 4

Si

P (Phosphorus atom) 4 3 3

P

S (Sulfur atom) 3 4 2

S

Cl (Chlorine atom) 2 3 1

Cl

Ar (Argon atom) 1 2 2

Ar

CH₃ (Methyl radical) 2 1 1

C1	0.0000	0.0000	0.0000
H2	1.0790	0.0000	0.0000
H3	-0.5395	-0.9344	0.0000
H4	-0.5395	0.9344	0.0000

CH₄ (Methane) 1 2 2

C1	0.0000	0.0000	0.0000
H2	0.6276	0.6276	0.6276
H3	0.6276	-0.6276	-0.6276
H4	-0.6276	0.6276	-0.6276
H5	-0.6276	-0.6276	0.6276

NH (Imidogen) (³Σ⁻) 3 2 2

N1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	1.0362

NH ₂ (Amino radical) 2 3 1				
N1	0.0000	0.0000	0.0000	
H2	0.0000	0.8036	0.6347	
H3	0.0000	-0.8036	0.6347	
NH ₃ (Ammonia) 1 2 2				
N1	0.0000	0.0000	0.0000	
H2	0.0000	-0.9377	-0.3816	
H3	0.8121	0.4689	-0.3816	
H4	-0.8121	0.4689	-0.3816	
OH (Hydroxyl radical) 2 3 1				
O1	0.0000	0.0000	0.0000	
H2	0.0000	0.0000	0.9697	
H ₂ O (Water) 1 2 2				
O1	0.0000	0.0000	0.1173	
H2	0.0000	0.7572	-0.4692	
H3	0.0000	-0.7572	-0.4692	
HF (Hydrogen fluoride) 1 2 2				
F1	0.0000	0.0000	0.0000	
H2	0.0000	0.0000	0.9168	
SiH ₃ (Silyl) 2 1 1				
Si1	0.0000	0.0000	0.0819	
H2	0.0000	1.3928	-0.3820	
H3	1.2062	-0.6964	-0.3820	
H4	-1.2062	-0.6964	-0.3820	
SiH ₄ (Silane) 1 2 2				
Si1	0.0000	0.0000	0.0000	
H2	0.8544	0.8544	0.8544	
H3	-0.8544	-0.8544	0.8544	
H4	-0.8544	0.8544	-0.8544	

H5	0.8544	-0.8544	-0.8544
<hr/>			
PH ₃ (Phosphine)	1	2	2
P1	0.0000	0.0000	0.0000
H2	0.0000	-1.1932	-0.7717
H3	1.0333	0.5966	-0.7717
H4	-1.0333	0.5966	-0.7717
<hr/>			
H ₂ S (Hydrogen sulfide)	1	2	2
S1	0.0000	0.0000	0.0000
H2	0.0000	0.9569	0.9208
H3	0.0000	-0.9569	0.9208
<hr/>			
HCl (Hydrogen chloride)	1	2	2
Cl1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	1.2746
<hr/>			
C ₂ H ₂ (Acetylene)	1	2	2
C1	0.0000	0.0000	0.6013
C2	0.0000	0.0000	-0.6013
H3	0.0000	0.0000	1.6644
H4	0.0000	0.0000	-1.6644
<hr/>			
C ₂ H ₄ (Ethylene)	1	2	2
C1	0.0000	0.0000	0.6695
C2	0.0000	0.0000	-0.6695
H3	0.0000	0.9289	1.2321
H4	0.0000	-0.9289	1.2321
H5	0.0000	0.9289	-1.2321
H6	0.0000	-0.9289	-1.2321
<hr/>			
C ₂ H ₆ (Ethane)	1	2	2
C1	0.0000	0.0000	0.7680
C2	0.0000	0.0000	-0.7680
H3	-1.0192	0.0000	1.1573

H4	0.5096	0.8826	1.1573
H5	0.5096	-0.8826	1.1573
H6	1.0192	0.0000	-1.1573
H7	-0.5096	-0.8826	-1.1573
H8	-0.5096	0.8826	-1.1573

HCN (Hydrogen cyanide) 1 2 2

C1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	1.0640
N3	0.0000	0.0000	-1.1560

CO (Carbon monoxide) 1 2 2

C1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.1283

HCO (Formyl radical) 2 1 1

C1	0.0000	0.0000	0.0000
H2	1.0800	0.0000	0.0000
O3	-0.5899	1.0427	0.0000

H₂CO (Formaldehyde) 1 2 2

O1	0.0000	0.0000	1.2050
C2	0.0000	0.0000	0.0000
H3	0.0000	0.9429	-0.5876
H4	0.0000	-0.9429	-0.5876

CH₃OH (Methyl alcohol) 1 2 2

C1	-0.0503	0.6685	0.0000
O2	-0.0503	-0.7585	0.0000
H3	-1.0807	1.0417	0.0000
H4	0.4650	1.0417	0.8924
H5	0.4650	1.0417	-0.8924
H6	0.8544	-1.0677	0.0000

N₂ (Nitrogen diatomic) 1 2 2

N1	0.0000	0.0000	0.5488
N2	0.0000	0.0000	-0.5488
<hr/>			
N ₂ H ₄ (Hydrazine)	1	2	2
N1	0.0000	0.7230	-0.1123
N2	0.0000	-0.7230	-0.1123
H3	-0.4470	1.0031	0.7562
H4	0.4470	-1.0031	0.7562
H5	0.9663	1.0031	0.0301
H6	-0.9663	-1.0031	0.0301
<hr/>			
NO (Nitric oxide)	2	1	3
O1	0.0000	0.0000	0.0000
N2	0.0000	0.0000	1.1508
<hr/>			
O ₂ (Oxygen diatomic) (³ Σ _g)	3	2	2
O1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.2075
<hr/>			
H ₂ O ₂ (Hydrogen peroxide)	1	2	2
O1	0.0000	0.7375	-0.0528
O2	0.0000	-0.7375	-0.0528
H3	0.8190	0.8170	0.4220
H4	-0.8190	-0.8170	0.4220
<hr/>			
F ₂ (Fluorine diatomic)	1	2	2
F1	0.0000	0.0000	0.0000
F2	0.0000	0.0000	1.4119
<hr/>			
CO ₂ (Carbon dioxide)	1	2	2
C1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.1621
O3	0.0000	0.0000	-1.1621
<hr/>			
P ₂ (Phosphorus diatomic)	1	2	2
P1	0.0000	0.0000	0.0000

P2	0.0000	0.0000	1.8934
<hr/>			
S ₂ (Sulfur diatomic) (³Σ _g)	3	2	2
S1	0.0000	0.0000	0.0000
S2	0.0000	0.0000	1.8892
<hr/>			
Cl ₂ (Chlorine diatomic)	1	2	2
Cl1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.9879
<hr/>			
NaCl (Sodium Chloride)	1	2	2
Na1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	2.3608
<hr/>			
SiO (Silicon monoxide)	1	2	2
Si1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.5097
<hr/>			
CS (Carbon monosulfide)	1	2	2
C1	0.0000	0.0000	0.0000
S2	0.0000	0.0000	1.5349
<hr/>			
ClO (Monochlorine monoxide)	2	3	1
O1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.5696
<hr/>			
ClF (Chlorine monofluoride)	1	2	2
F1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.6283
<hr/>			
Si ₂ H ₆ (Disilane)	1	2	2
Si1	0.0000	0.0000	1.1600
Si2	0.0000	0.0000	-1.1600
H3	0.0000	1.3865	1.6483
H4	-1.2008	-0.6933	1.6483
H5	1.2008	-0.6933	1.6483
H6	0.0000	-1.3865	-1.6483

H7	-1.2008	0.6933	-1.6483
H8	1.2008	0.6933	-1.6483
<hr/>			
CH ₃ Cl (Methyl chloride)	1 2 2		
C1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.7810
H3	1.0424	0.0000	-0.3901
H4	-0.5212	0.9027	-0.3901
H5	-0.5212	-0.9027	-0.3901
<hr/>			
CH ₃ SH (Methanethiol)	1 2 2		
C1	-0.8500	-0.0344	-0.2000
S2	0.9000	-0.5125	-0.1219
H3	1.4219	0.5781	0.4250
H4	-0.9406	0.8688	-0.8219
H5	-1.4219	-0.8688	-0.6469
H6	-1.2031	0.1656	0.8219
<hr/>			
SO ₂ (Sulfur dioxide)	1 2 2		
S1	0.0000	0.0000	0.0000
O2	0.0000	1.2371	0.7215
O3	0.0000	-1.2371	0.7215
<hr/>			
BF ₃ (Borane, trifluoro-)	1 2 2		
B1	0.0000	0.0000	0.0000
F2	0.0000	1.3070	0.0000
F3	1.1319	-0.6535	0.0000
F4	-1.1319	-0.6535	0.0000
<hr/>			
BCl ₃ (Borane, trichloro-)	1 2 2		
B1	0.0000	0.0000	0.0000
Cl2	0.0000	1.7421	0.0000
Cl3	1.5087	-0.8711	0.0000
Cl4	-1.5087	-0.8711	0.0000
<hr/>			

AlCl ₃ (Aluminum trichloride)	1	2	2			
Al1	0.0000			0.0000		0.0000
Cl2	0.0000			2.0600		0.0000
Cl3	1.7840			-1.0300		0.0000
Cl4	-1.7840			-1.0300		0.0000
CF ₄ (Carbon tetrafluoride)	1	2	2			
C1	0.0000			0.0000		0.0000
F2	0.7593			0.7593		0.7593
F3	-0.7593			-0.7593		0.7593
F4	-0.7593			0.7593		-0.7593
F5	0.7593			-0.7593		-0.7593
CCl ₄ (Carbon tetrachloride)	1	2	2			
C1	0.0000			0.0000		0.0000
Cl2	1.0202			1.0202		1.0202
Cl3	-1.0202			-1.0202		1.0202
Cl4	-1.0202			1.0202		-1.0202
Cl5	1.0202			-1.0202		-1.0202
OCS (Carbonyl sulfide)	1	2	2			
C1	0.0000			0.0000		0.0000
O2	0.0000			0.0000		1.1600
S3	0.0000			0.0000		-1.5600
CS ₂ (Carbon disulfide)	1	2	2			
C1	0.0000			0.0000		0.0000
S2	0.0000			0.0000		1.5540
S3	0.0000			0.0000		-1.5540
CF ₂ O (Carbonic difluoride)	1	2	2			
O1	0.0000			0.0000		1.3143
C2	0.0000			0.0000		0.1403
F3	0.0000			1.0614		-0.6309

F4	0.0000	-1.0614	-0.6309
<hr/>			
SiF ₄ (Silicon tetrafluoride)	1 2 2		
Si1	0.0000	0.0000	0.0000
F2	0.8972	0.8972	0.8972
F3	-0.8972	-0.8972	0.8972
F4	-0.8972	0.8972	-0.8972
F5	0.8972	-0.8972	-0.8972
<hr/>			
N ₂ O (Nitrous oxide)	1 2 2		
N1	0.0000	0.0000	-1.1998
N2	0.0000	0.0000	-0.0716
O3	0.0000	0.0000	1.1126
<hr/>			
NF ₃ (Nitrogen trifluoride)	1 2 2		
N1	0.0000	0.0000	0.4731
F2	0.0000	1.2279	-0.1226
F3	1.0634	-0.6140	-0.1226
F4	-1.0634	-0.6140	-0.1226
<hr/>			
PF ₃ (Phosphorus trifluoride)	1 2 2		
P1	0.0000	0.0000	0.4602
F2	0.0000	1.3578	-0.2557
F3	1.1759	-0.6789	-0.2557
F4	-1.1759	-0.6789	-0.2557
<hr/>			
O ₃ (Ozone)	1 2 2		
O1	0.0000	0.0000	0.0000
O2	0.0000	1.0885	0.6697
O3	0.0000	-1.0885	0.6697
<hr/>			
F ₂ O (Difluorine monoxide)	1 2 2		
O1	0.0000	0.0000	0.6074
F2	0.0000	1.1063	-0.2700
F3	0.0000	-1.1063	-0.2700
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ClF ₃ (Chlorine trifluoride)	1	2	2	
Cl1		0.0000	0.0000	0.3572
F2		0.0000	0.0000	-1.2408
F3		0.0000	1.6964	0.2831
F4		0.0000	-1.6964	0.2831
<hr/>				
C ₂ F ₄ (Tetrafluoroethylene)	1	2	2	
C1		0.0000	0.0000	0.6555
C2		0.0000	0.0000	-0.6555
F3		0.0000	1.0961	1.3893
F4		0.0000	-1.0961	1.3893
F5		0.0000	-1.0961	-1.3893
F6		0.0000	1.0961	-1.3893
<hr/>				
CF ₃ CN (Acetonitrile, trifluoro-)	1			
C1		0.0000	0.0000	-0.3406
C2		0.0000	0.0000	1.1518
N3		0.0000	0.0000	2.3054
F4		0.0000	1.2540	-0.7780
F5		1.0860	-0.6270	-0.7780
F6		-1.0860	-0.6270	-0.7780
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CH ₃ CCH (Propyne)	1	2	2	
C1		0.0000	0.0000	-1.2455
C2		0.0000	0.0000	0.2135
C3		0.0000	0.0000	1.4195
H4		0.0000	0.0000	2.4755
H5		0.0000	1.0465	-1.6003
H6		0.9063	-0.5232	-1.6003
H7		-0.9063	-0.5232	-1.6003
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CH ₂ CCH ₂ (Allene)	1	2	2	
C1		0.0000	0.0000	0.0000

C2	0.0000	0.0000	1.3080
C3	0.0000	0.0000	-1.3080
H4	0.0000	0.9327	1.8662
H5	0.0000	-0.9327	1.8662
H6	0.9327	0.0000	-1.8662
H7	-0.9327	0.0000	-1.8662

C₃H₄ (Cyclopropene) 1 2 2

C1	0.0000	0.0000	0.8628
C2	0.0000	0.6476	-0.5001
C3	0.0000	-0.6476	-0.5001
H4	0.0000	1.5745	-1.0386
H5	0.0000	-1.5745	-1.0386
H6	0.9154	0.0000	1.4509
H7	-0.9154	0.0000	1.4509

C₃H₆ (Cyclopropane) 1 2 2

C1	0.0000	0.8666	0.0000
C2	0.7505	-0.4333	0.0000
C3	-0.7505	-0.4333	0.0000
H4	0.0000	1.4525	0.9108
H5	1.2579	-0.7262	0.9108
H6	-1.2579	-0.7262	0.9108
H7	0.0000	1.4525	-0.9108
H8	1.2579	-0.7262	-0.9108
H9	-1.2579	-0.7262	-0.9108

C₃H₈ (Propane) 1

C1	0.0000	0.5863	-0.0000
C2	-1.2681	-0.2626	0.0000
C3	1.2681	-0.2626	-0.0000
H4	0.0000	1.2449	0.8760

H5	-0.0003	1.2453	-0.8758
H6	-2.1576	0.3742	0.0000
H7	2.1576	0.3743	-0.0000
H8	-1.3271	-0.9014	0.8800
H9	-1.3271	-0.9014	-0.8800
H10	1.3271	-0.9014	-0.8800
H11	1.3272	-0.9014	0.8800

CH₃CCCH₃ (2-Butyne) 1

C1	0.0000	0.0000	0.6070
C2	0.0000	0.0000	-0.6070
C3	0.0000	0.0000	2.0750
C4	0.0000	0.0000	-2.0750
H5	0.0000	1.0440	2.4695
H6	-0.9041	-0.5220	2.4695
H7	0.9041	-0.5220	2.4695
H8	0.0000	1.0440	-2.4695
H9	0.9041	-0.5220	-2.4695
H10	-0.9041	-0.5220	-2.4695

C₄H₆ (Cyclobutene) 1

C1	0.0000	0.6710	0.8107
C2	0.0000	-0.6710	0.8107
C3	0.0000	0.7821	-0.7023
C4	0.0000	-0.7821	-0.7023
H5	0.0000	1.4165	1.5962
H6	0.0000	-1.4165	1.5962
H7	0.8986	1.2425	-1.1233
H8	-0.8986	-1.2425	-1.1233
H9	-0.8986	1.2425	-1.1233
H10	0.8986	-1.2425	-1.1233

 $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ (Isobutane) 1

C1	0.0000	0.0000	0.3650
H2	0.0000	0.0000	1.4730
C3	0.0000	1.4528	-0.0987
C4	1.2582	-0.7264	-0.0987
C5	-1.2582	-0.7264	-0.0987
H6	0.0000	1.4867	-1.1931
H7	1.2875	-0.7433	-1.1931
H8	-1.2875	-0.7433	-1.1931
H9	0.8941	1.9575	0.2821
H10	-0.8941	1.9575	0.2821
H11	1.2482	-1.7530	0.2821
H12	2.1422	-0.2045	0.2821
H13	-2.1422	-0.2045	0.2821
H14	-1.2482	-1.7530	0.2821

 C_6H_6 (Benzene) 1

C1	0.0000	1.3970	0.0000
C2	1.2098	0.6985	0.0000
C3	1.2098	-0.6985	0.0000
C4	0.0000	-1.3970	0.0000
C5	-1.2098	-0.6985	0.0000
C6	-1.2098	0.6985	0.0000
H7	0.0000	2.4810	0.0000
H8	2.1486	1.2405	0.0000
H9	2.1486	-1.2405	0.0000
H10	0.0000	-2.4810	0.0000
H11	-2.1486	-1.2405	0.0000
H12	-2.1486	1.2405	0.0000

 CH_2F_2 (Methane, difluoro-) 1 2 2

C1	0.0000	0.0000	0.5003
H2	-0.9029	0.0000	1.1002
H3	0.9029	0.0000	1.1002
F4	0.0000	1.0962	-0.2890
F5	0.0000	-1.0962	-0.2890

CHF₃ (Methane, trifluoro-) 1 2 2

C1	0.0000	0.0000	0.3086
H2	0.0000	0.0000	1.4066
F3	0.0000	1.2609	-0.1207
F4	1.0920	-0.6305	-0.1207
F5	-1.0920	-0.6305	-0.1207

CH₂Cl₂ (Methylene chloride) 1 2 2

C1	0.0000	0.0000	0.7761
H2	-0.8854	0.0000	1.3734
H3	0.8854	0.0000	1.3734
Cl4	0.0000	1.4675	-0.2178
Cl5	0.0000	-1.4675	-0.2178

CHCl₃ (Chloroform) 1 2 2

C1	0.0000	0.0000	0.5231
H2	0.0000	0.0000	1.5961
Cl3	0.0000	1.6562	-0.0928
Cl4	1.4343	-0.8281	-0.0928
Cl5	-1.4343	-0.8281	-0.0928

CH₃NO₂ (Methane, nitro-) 1 2 2

C1	1.4008	0.0000	0.0000
N2	-0.0878	0.0000	0.0000
H3	1.7215	-1.0392	0.0000
H4	1.7215	0.5196	0.9000
H5	1.7215	0.5196	-0.9000

O6	-0.6498	1.0874	0.0000
O7	-0.6498	-1.0874	0.0000
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CH ₃ SiH ₃ (Methyl silane)	1 2 2		
C1	0.0000	0.0000	-1.2367
Si2	0.0000	0.0000	0.6319
H3	0.0000	-1.0237	-1.6272
H4	-0.8866	0.5119	-1.6272
H5	0.8866	0.5119	-1.6272
H6	0.0000	1.3893	1.1514
H7	-1.2031	-0.6946	1.1514
H8	1.2031	-0.6946	1.1514
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HCOOH (Formic acid)	1 2 2		
C1	0.0000	0.4199	0.0000
O2	-1.0543	-0.4121	0.0000
O3	1.1506	0.0721	0.0000
H4	-0.0799	1.5140	0.0000
H5	-0.6905	-1.3134	0.0000
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CH ₃ CONH ₂ (Acetamide)	1 2 2		
C1	-1.3674	-0.3302	0.0013
C2	0.0720	0.1552	-0.0019
N3	1.0259	-0.8416	-0.0326
O4	0.3726	1.3376	0.0057
H5	-2.0656	0.5484	-0.0612
H6	-1.5426	-1.0080	-0.8780
H7	-1.5719	-0.9088	0.9430
H8	2.0050	-0.5675	0.0710
H9	0.7853	-1.8244	0.1113
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C ₂ H ₅ N (Aziridine)	1		
N1	-0.0037	0.8559	-0.1934

H2	-0.0140	1.4040	0.6620
C3	-0.7380	-0.4043	0.0261
C4	0.7425	-0.3952	0.0380
H5	-1.2757	-0.4486	0.9652
H6	-1.2332	-0.8641	-0.8216
H7	1.2820	-0.7584	-0.8280
H8	1.2404	-0.5270	0.9918

C₂N₂ (Cyanogen) 1 2 2

C1	0.0000	0.0000	0.6950
C2	0.0000	0.0000	-0.6950
N3	0.0000	0.0000	1.8450
N4	0.0000	0.0000	-1.8450

CH₃NHCH₃ (Dimethylamine) 1

N1	0.0934	-0.5520	0.0000
H2	-0.6454	-1.2544	0.0000
C3	-0.0220	0.2554	1.2139
C4	-0.0220	0.2554	-1.2139
H5	-0.9221	0.8833	1.2437
H6	-0.9221	0.8833	-1.2437
H7	0.8440	0.9287	1.2609
H8	0.8440	0.9287	-1.2609
H9	-0.0138	-0.3909	2.0843
H10	-0.0138	-0.3909	-2.0843

CH₂CO (Ketene) 1 2 2

C1	0.0000	0.0000	0.0000
C2	0.0000	0.0000	1.3150
O3	0.0000	0.0000	2.4750
H4	0.0000	0.9451	-0.5206
H5	0.0000	-0.9451	-0.5206

C ₂ H ₄ O (Ethylene oxide)	1	2	2		
O1		0.0000		0.0000	0.8517
C2		0.0000		0.7297	-0.3725
C3		0.0000		-0.7297	-0.3725
H4		-0.9230		1.2565	-0.5859
H5		0.9230		1.2565	-0.5859
H6		0.9230		-1.2565	-0.5859
H7		-0.9230		-1.2565	-0.5859
C ₂ H ₂ O ₂ (Ethanedial)	1	2	2		
C1		0.0000		0.7630	0.0000
C2		0.0000		-0.7630	0.0000
H3		1.0481		1.1907	0.0000
H4		-1.0481		-1.1907	0.0000
O5		-1.0367		1.3908	0.0000
O6		1.0367		-1.3908	0.0000
CH ₃ CH ₂ OH (Ethanol)	1	2	2		
C1		1.1879		-0.3829	0.0000
C2		0.0000		0.5526	0.0000
O3		-1.1867		-0.2472	0.0000
H4		-1.9237		0.3850	0.0000
H5		2.0985		0.2306	0.0000
H6		1.1184		-1.0093	0.8869
H7		1.1184		-1.0093	-0.8869
H8		-0.0227		1.1812	0.8852
H9		-0.0227		1.1812	-0.8852
CH ₃ OCH ₃ (Dimethyl ether)	1	2	2		
O1		0.0000		0.0000	0.5952
C2		0.0000		1.1669	-0.1963
C3		0.0000		-1.1669	-0.1963

H4	0.0000	2.0489	0.4542
H5	0.0000	-2.0489	0.4542
H6	0.8950	1.1787	-0.8287
H7	-0.8950	1.1787	-0.8287
H8	-0.8950	-1.1787	-0.8287
H9	0.8950	-1.1787	-0.8287

C₂H₄S (Thiirane) 1 2 2

S1	0.0000	0.0000	0.8622
C2	0.0000	0.7421	-0.7942
C3	0.0000	-0.7421	-0.7942
H4	-0.9174	1.2493	-1.0661
H5	0.9174	1.2493	-1.0661
H6	0.9174	-1.2493	-1.0661
H7	-0.9174	-1.2493	-1.0661

CH₃SOCH₃ (Dimethyl sulfoxide) 1

S1	0.0000	0.1432	0.4202
O2	0.0000	1.4024	-0.3667
C3	1.3425	-0.8664	-0.2227
C4	-1.3425	-0.8664	-0.2227
H5	2.2553	-0.4311	0.0751
H6	-2.2553	-0.4311	0.0751
H7	1.3057	-1.8579	0.2349
H8	1.2255	-0.9383	-1.3113
H9	-1.3057	-1.8579	0.2349
H10	-1.2255	-0.9383	-1.3113

CH₂CHF (Ethene, fluoro-) 1 2 2

C1	0.0000	0.4476	0.0000
C2	1.1877	-0.1487	0.0000
F3	-1.1356	-0.2769	0.0000

H4	-0.2349	1.5038	0.0000
H5	1.2321	-1.2348	0.0000
H6	2.0966	0.4290	0.0000

CH₃CH₂Cl (Ethyl chloride) 1 2 2

C1	1.5949	-0.3563	-0.0000
C2	0.4757	0.6568	-0.0004
H3	2.5527	0.1648	0.0000
H4	1.5351	-0.9919	-0.8828
H5	1.5347	-0.9917	0.8828
Cl6	-1.1206	-0.1505	-0.0005
H7	0.5089	1.2945	-0.8790
H8	0.4949	1.2796	0.8893

CH₂CHCl (Ethene, chloro-) 1 2 2

C1	0.0000	0.0000	1.3320
C2	0.0000	0.0000	0.0000
Cl3	0.0000	1.4589	2.2543
H4	0.0000	-0.9058	1.9384
H5	0.0000	0.9249	-0.5557
H6	0.0000	-0.9391	-0.5313

CH₃COCl (Acetyl Chloride) 1 2 2

C1	0.0000	0.5272	0.0000
C2	1.4961	0.6994	0.0000
O3	-0.8349	1.3710	0.0000
Cl4	-0.4665	-1.2092	0.0000
H5	1.7591	1.7726	0.0000
H6	1.9367	0.2285	0.8973
H7	1.9367	0.2285	-0.8973

CH₂ClCH₂CH₃ (Propane, 1-chloro-) 1

Cl1	1.7375	0.1388	0.0000
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C2	0.0000	0.5937	0.0000
H3	-0.1639	1.2199	0.9054
H4	-0.1639	1.2199	-0.9054
C5	-0.8957	-0.6405	0.0000
H6	-0.6638	-1.2607	0.8947
H7	-0.6638	-1.2607	-0.8947
C8	-2.3710	-0.2543	0.0000
H9	-2.6338	0.3458	0.8998
H10	-2.6338	0.3458	-0.8998
H11	-3.0133	-1.1633	0.0000

N(CH₃)₃ (Trimethylamine) 1

N1	0.0000	-0.0000	-0.3852
C2	-0.9758	-0.9757	0.0634
C3	1.3330	-0.3571	0.0634
C4	-0.3572	1.3328	0.0634
H5	-1.0253	-1.0252	1.1492
H6	1.4006	-0.3752	1.1492
H7	-0.3753	1.4004	1.1492
H8	-1.9833	-0.7091	-0.3156
H9	-0.7093	-1.9833	-0.3156
H10	1.6060	-1.3629	-0.3156
H11	2.0722	0.3776	-0.3156
H12	0.3774	2.0722	-0.3156
H13	-1.3631	1.6057	-0.3156

C₄H₄O (Furan) 1

O1	0.0000	0.0000	1.1626
C2	0.0000	1.0920	0.3487
C3	0.0000	-1.0920	0.3487
C4	0.0000	0.7169	-0.9596

C5	0.0000	-0.7169	-0.9596
H6	0.0000	2.0473	0.8439
H7	0.0000	-2.0473	0.8439
H8	0.0000	1.3509	-1.8290
H9	0.0000	-1.3509	-1.8290

C₄H₅N (Pyrrole) 1

N1	0.0000	0.0000	1.1218
H2	0.0000	0.0000	2.1178
C3	0.0000	1.1209	0.3341
C4	0.0000	-1.1209	0.3341
C5	0.0000	0.7076	-0.9847
C6	0.0000	-0.7076	-0.9847
H7	0.0000	2.1084	0.7614
H8	0.0000	-2.1084	0.7614
H9	0.0000	1.3566	-1.8429
H10	0.0000	-1.3566	-1.8429

NO₂ (Nitrogen dioxide) 2 1 1

N1	0.0000	0.0000	0.0000
O2	0.0000	1.0989	0.4653
O3	0.0000	-1.0989	0.4653

SF₆ (Sulfur Hexafluoride) 1

S1	0.0000	0.0000	0.0000
F2	0.0000	0.0000	1.5607
F3	0.0000	1.5607	0.0000
F4	1.5607	0.0000	0.0000
F5	0.0000	-1.5607	0.0000
F6	-1.5607	0.0000	0.0000
F7	0.0000	0.0000	-1.5607

CFCl₃ (Trichloromonofluoromethane) 1 2 2

C1	0.0000	0.0000	0.2472
F2	0.0000	0.0000	1.5922
Cl3	0.0000	1.6732	-0.3101
Cl4	1.4491	-0.8366	-0.3101
Cl5	-1.4491	-0.8366	-0.3101

CF₃Cl (Methane, chlorotrifluoro-) 1 2 2

C1	0.0000	0.0000	-0.3471
Cl2	0.0000	0.0000	1.4049
F3	0.0000	1.2425	-0.8074
F4	1.0760	-0.6212	-0.8074
F5	-1.0760	-0.6212	-0.8074

CF₃Br (Bromotrifluoromethane) 1

C1	0.0000	0.0000	-0.8088
Br2	0.0000	0.0000	1.1146
F3	0.0000	1.2455	-1.2651
F4	1.0787	-0.6228	-1.2651
F5	-1.0787	-0.6228	-1.2651

HCCF (Fluoroacetylene) 1 2 2

C1	0.0000	0.0000	-0.0942
C2	0.0000	0.0000	-1.2922
F3	0.0000	0.0000	1.1848
H4	0.0000	0.0000	-2.3452

HCCCN (Cyanoacetylene) 1 2 2

N1	0.0000	0.0000	1.9018
C2	0.0000	0.0000	0.7413
C3	0.0000	0.0000	-0.6351
C4	0.0000	0.0000	-1.8409
H5	0.0000	0.0000	-2.9033

C₄N₂ (2-Butynedinitrile) 1 2 2

C1	0.0000	0.0000	2.5100
C2	0.0000	0.0000	3.7000
C3	0.0000	0.0000	1.1400
C4	0.0000	0.0000	5.0700
N5	0.0000	0.0000	0.0000
N6	0.0000	0.0000	6.2100

C₂N₂ (Cyanogen) 1 2 2

C1	0.0000	0.0000	0.6950
C2	0.0000	0.0000	-0.6950
N3	0.0000	0.0000	1.8450
N4	0.0000	0.0000	-1.8450

C₃O₂ (Carbon suboxide) 1 2 2

C1	0.0000	0.0000	0.0308
C2	0.0000	1.2509	0.0123
C3	0.0000	-1.2509	0.0123
O4	0.0000	2.3964	-0.0207
O5	0.0000	-2.3964	-0.0207

FCN (Cyanogen fluoride) 1 2 2

C1	0.0000	0.0000	0.0000
F2	0.0000	0.0000	-1.2620
N3	0.0000	0.0000	1.1590

C₄H₂ (Diacetylene) 1 2 2

C1	0.0000	0.0000	0.6890
C2	0.0000	0.0000	-0.6890
C3	0.0000	0.0000	1.8940
C4	0.0000	0.0000	-1.8940
H5	0.0000	0.0000	2.9520
H6	0.0000	0.0000	-2.9520

H₂CS (Thioformaldehyde) 1 2 2

S1	0.0000	0.0000	0.5846
C2	0.0000	0.0000	-1.0262
H3	0.0000	0.9244	-1.5980
H4	0.0000	-0.9244	-1.5980

CHONH₂ (Formamide) 1 2 2

C1	0.0000	0.4165	0.0000
O2	1.1942	0.2217	0.0000
N3	-0.9373	-0.5551	0.0000
H4	-0.4299	1.4182	0.0000
H5	-0.6608	-1.5171	0.0000
H6	-1.9020	-0.2881	0.0000

CH₂CHCHO (Acrolein) 1

C1	-0.1496	-0.7423	0.0000
C2	0.0000	0.7200	0.0000
C3	1.2291	1.2662	0.0000
O4	-1.2313	-1.3044	0.0000
H5	0.8007	-1.3120	0.0000
H6	-0.9066	1.3142	0.0000
H7	1.3716	2.3428	0.0000
H8	2.1072	0.6273	0.0000

CH₂CCl₂ (Ethene, 1,1-dichloro-) 1 2 2

C1	0.0000	0.0000	1.7363
C2	0.0000	0.0000	0.4123
H3	0.0000	0.9266	2.2713
H4	0.0000	-0.9266	2.2713
Cl5	0.0000	1.4382	-0.5128
Cl6	0.0000	-1.4382	-0.5128

C₂HF₃ (Trifluoroethylene) 1 2 2

C1	0.0000	0.4436	0.0000
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C2	-0.7139	-0.6916	0.0000
F3	1.3153	0.4857	0.0000
F4	-0.5506	1.6388	0.0000
F5	-0.0873	-1.8784	0.0000
H6	-1.8133	-0.7269	0.0000

CH₂CF₂ (Ethene, 1,1-difluoro-) 1 2 2

C1	0.0000	0.0000	1.3851
C2	0.0000	0.0000	0.0701
H3	0.0000	0.9419	1.9094
H4	0.0000	-0.9419	1.9094
F5	0.0000	1.0777	-0.6972
F6	0.0000	-1.0777	-0.6972

CH₃F (Methyl fluoride) 1 2 2

C1	0.0000	0.0000	-0.6289
F2	0.0000	0.0000	0.7541
H3	0.0000	1.0201	-1.0043
H4	0.8835	-0.5101	-1.0043
H5	-0.8835	-0.5101	-1.0043

CF₂Cl₂ (Difluorodichloromethane) 1 2 2

C1	0.0000	0.0000	0.3171
F2	0.0000	1.0758	1.1243
F3	0.0000	-1.0758	1.1243
Cl4	1.4505	0.0000	-0.6512
Cl5	-1.4505	0.0000	-0.6512

SiF₂ (Silicon difluoride) 1 2 2

Si1	0.0000	0.0000	0.5703
F2	0.0000	1.2249	-0.4436
F3	0.0000	-1.2249	-0.4436

TABLE XVII. Atomic energies (in kcal/mol) from the H atom to the Ar atom [58].

Atom	Reference	ω M05-D	M05-2X	ω B97X-D
H	-313.76	-311.52	-313.31	-315.51
He	-1822.12	-1822.11	-1823.25	-1824.57
Li	-4692.56	-4693.72	-4694.37	-4699.80
Be	-9203.92	-9198.97	-9204.50	-9202.60
B	-15470.58	-15466.17	-15471.98	-15468.00
C	-23748.12	-23746.17	-23752.06	-23745.12
N	-34255.28	-34254.32	-34260.32	-34251.37
O	-47105.50	-47107.44	-47113.72	-47103.64
F	-62584.04	-62587.59	-62593.80	-62583.06
Ne	-80909.66	-80910.31	-80917.57	-80906.81
Na	-101816.42	-101814.09	-101820.46	-101818.06
Mg	-125535.30	-125538.45	-125549.12	-125538.97
Al	-152074.59	-152077.17	-152084.44	-152078.77
Si	-181575.73	-181577.53	-181581.20	-181577.86
P	-214143.51	-214141.04	-214140.76	-214140.27
S	-249818.09	-249817.74	-249815.58	-249817.21
Cl	-288747.57	-288747.04	-288743.15	-288746.55
Ar	-331036.74	-331035.35	-331028.07	-331036.25
MSE		0.37	-3.01	-0.05
MAE		2.02	5.10	2.51
rms		2.42	6.31	2.96

TABLE XVIII. Non-hydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set [63].

Reactions		ΔE_{ref}	ω M05-D	M05-2X	ω B97X-D
Heavy-atom transfer reactions					
$H + N_2O \rightarrow OH + N_2$	V^f	18.14	16.52	18.82	17.47
	V^r	83.22	80.54	85.45	77.75
$H + FH \rightarrow HF + H$	V^f	42.18	38.34	41.16	40.56
	V^r	42.18	38.34	41.16	40.56
$H + ClH \rightarrow HCl + H$	V^f	18.00	17.83	19.64	18.19
	V^r	18.00	17.83	19.64	18.19
$H + FCH_3 \rightarrow HF + CH_3$	V^f	30.38	28.76	31.70	30.02
	V^r	57.02	54.26	55.28	54.47
$H + F_2 \rightarrow HF + F$	V^f	2.27	-0.07	2.90	-0.60
	V^r	106.18	106.50	114.64	103.96
$CH_3 + FCl \rightarrow CH_3F + Cl$	V^f	7.43	4.22	4.04	2.76
	V^r	60.17	57.63	59.94	56.55
Nucleophilic substitution reactions					
$F^- + CH_3F \rightarrow FCH_3 + F^-$	V^f	-0.34	-1.79	-1.93	-1.37
	V^r	-0.34	-1.79	-1.93	-1.37
$F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$	V^f	13.38	12.98	14.01	12.85
	V^r	13.38	12.98	14.01	12.85
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	V^f	3.10	2.29	0.75	3.70
	V^r	3.10	2.29	0.75	3.70
$Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$	V^f	13.61	12.85	12.01	14.30
	V^r	13.61	12.85	12.01	14.30
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	V^f	-12.54	-14.38	-15.89	-13.58
	V^r	20.11	21.65	21.86	21.26
$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	V^f	2.89	2.41	2.13	3.07
	V^r	29.62	31.11	31.97	30.50
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	V^f	-2.78	-3.96	-4.22	-3.31
	V^r	17.33	16.05	15.54	17.90
$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	V^f	10.96	10.32	11.14	10.57
	V^r	47.20	49.33	48.84	49.20
Unimolecular and association reactions					
$H + N_2 \rightarrow HN_2$	V^f	14.69	11.94	14.65	12.32
	V^r	10.72	12.01	13.07	13.40
$H + CO \rightarrow HCO$	V^f	3.17	2.91	4.96	3.37
	V^r	22.68	24.38	25.23	26.20
$H + C_2H_4 \rightarrow CH_3CH_2$	V^f	1.72	2.46	3.68	3.03
	V^r	41.75	44.44	44.88	45.37
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	V^f	6.85	4.13	4.09	4.57
	V^r	32.97	33.17	32.57	33.85
$HCN \rightarrow HNC$	V^f	48.16	44.78	46.45	46.42
	V^r	33.11	31.56	33.10	33.27
MSE			-0.94	0.13	-0.45
MAE			1.57	1.75	1.51
rms			1.89	2.24	2.00

TABLE XIX. Hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set [15, 63].

Reactions		ΔE_{ref}	ω M05-D	M05-2X	ω B97X-D
H + HCl→H ₂ + Cl	V^f	5.7	3.61	4.82	4.08
	V^r	8.7	4.68	5.94	4.58
OH + H ₂ →H + H ₂ O	V^f	5.1	1.94	4.61	2.22
	V^r	21.2	18.69	21.90	18.77
CH ₃ + H ₂ →H + CH ₄	V^f	12.1	9.14	11.72	9.06
	V^r	15.3	13.35	16.07	13.54
OH + CH ₄ →CH ₃ + H ₂ O	V^f	6.7	2.53	4.69	3.04
	V^r	19.6	15.06	17.64	15.11
H + H ₂ →H ₂ + H	V^f	9.6	8.83	12.66	9.21
	V^r	9.6	8.83	12.66	9.21
OH + NH ₃ →H ₂ O + NH ₂	V^f	3.2	-0.14	2.67	-0.02
	V^r	12.7	9.73	12.41	9.69
HCl + CH ₃ →Cl + CH ₄	V^f	1.7	-1.60	-1.30	-1.86
	V^r	7.9	3.69	4.17	3.11
OH + C ₂ H ₆ →H ₂ O + C ₂ H ₅	V^f	3.4	-0.28	2.19	0.17
	V^r	19.9	16.88	19.24	16.57
F + H ₂ →HF + H	V^f	1.8	-2.22	0.10	-3.70
	V^r	33.4	30.78	33.40	29.01
O + CH ₄ →OH + CH ₃	V^f	13.7	8.85	10.62	9.20
	V^r	8.1	4.39	5.50	4.67
H + PH ₃ →PH ₂ + H ₂	V^f	3.1	2.21	4.25	3.28
	V^r	23.2	23.45	25.62	23.46
H + HO→H ₂ + O	V^f	10.7	7.90	10.38	8.84
	V^r	13.1	8.15	11.16	8.89
H + H ₂ S→H ₂ + HS	V^f	3.5	3.24	5.42	4.05
	V^r	17.3	16.10	18.21	16.31
O + HCl→OH + Cl	V^f	9.8	4.95	7.01	5.47
	V^r	10.4	5.78	7.35	5.91
NH ₂ + CH ₃ →CH ₄ + NH	V^f	8.0	5.41	7.10	5.65
	V^r	22.4	18.17	20.33	18.41
NH ₂ + C ₂ H ₅ →C ₂ H ₆ + NH	V^f	7.5	7.09	8.56	7.26
	V^r	18.3	15.22	17.68	15.69
C ₂ H ₆ + NH ₂ →NH ₃ + C ₂ H ₅	V^f	10.4	7.97	10.11	8.60
	V^r	17.4	15.26	17.42	15.29
NH ₂ + CH ₄ →CH ₃ + NH ₃	V^f	14.5	10.81	12.71	11.28
	V^r	17.8	13.47	15.91	13.65
s-trans cis-C ₅ H ₈ →s-trans cis-C ₅ H ₈	V^f	38.4	37.23	39.06	39.07
	V^r	38.4	37.23	39.06	39.07
MSE			-2.82	-0.65	-2.57
MAE			2.83	1.51	2.70
rms			3.16	1.83	3.10

TABLE XX. Interaction energies (in kcal/mol) for the S22 set with new reference values. [70] The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included.

Complex [Symmetry]	ΔE_{ref}	ω M05-D	M05-2X	ω B97X-D
Hydrogen bonded complexes				
(NH ₃) ₂ [C _{2h}]	-3.133	-3.00	-3.12	-3.08
(H ₂ O) ₂ [C _s]	-4.989	-4.89	-5.08	-4.97
Formic acid dimer [C _{2h}]	-18.753	-18.98	-19.41	-19.28
Formamide dimer [C _{2h}]	-16.062	-15.65	-15.81	-16.17
Uracil dimer [C _{2h}]	-20.641	-19.90	-19.64	-20.43
2-pyridoxine·2-aminopyridine [C ₁]	-16.934	-16.40	-15.36	-17.06
Adenine·thymine WC [C ₁]	-16.660	-15.87	-14.84	-16.46
MSE		0.35	0.56	-0.04
MAE		0.42	0.77	0.18
Dispersion complexes				
(CH ₄) ₂ [D _{3d}]	-0.527	-0.65	-0.51	-0.57
(C ₂ H ₄) ₂ [D _{2d}]	-1.472	-1.70	-1.42	-1.79
Benzene·CH ₄ [C ₃]	-1.448	-1.68	-1.13	-1.70
Benzene dimer [C _{2h}]	-2.654	-3.55	-1.38	-3.16
Pyrazine dimer [C _s]	-4.255	-4.40	-2.95	-4.27
Uracil dimer [C ₂]	-9.805	-9.83	-8.32	-9.79
Indole·benzene [C ₁]	-4.524	-5.47	-2.57	-5.10
Adenine·thymine stack [C ₁]	-11.730	-12.00	-9.40	-11.86
MSE		-0.36	1.09	-0.23
MAE		0.36	1.09	0.23
Mixed complexes				
Ethene·ethine [C _{2v}]	-1.496	-1.52	-1.44	-1.63
Benzene·H ₂ O [C _s]	-3.275	-3.60	-3.57	-3.50
Benzene·NH ₃ [C _s]	-2.312	-2.54	-2.23	-2.53
Benzene·HCN [C _s]	-4.541	-4.76	-4.90	-4.79
Benzene dimer [C _{2v}]	-2.717	-2.88	-1.97	-2.89
Indole·benzene T-shape [C ₁]	-5.627	-5.85	-4.76	-5.64
Phenol dimer [C ₁]	-7.097	-6.89	-6.03	-6.99
MSE		-0.14	0.31	-0.13
MAE		0.20	0.50	0.16
MSE		-0.06	0.67	-0.14
MAE		0.33	0.80	0.19
rms		0.42	1.06	0.25

TABLE XXI. Comparison of errors of different functionals for the reaction energies (in kcal/mol) of the 30 chemical reactions in the NHTBH38/04 and HTBH38/04 database [15, 63].

Reactions	ΔE_{ref}	ω M05-D	M05-2X	ω B97X-D
$H + N_2O \rightarrow OH + N_2$	-65.08	-64.03	-66.63	-60.28
$H + FCH_3 \rightarrow HF + CH_3$	-26.64	-25.50	-23.58	-24.44
$H + F_2 \rightarrow HF + F$	-103.91	-106.58	-111.74	-104.56
$CH_3 + FCl \rightarrow CH_3F + Cl$	-52.74	-53.41	-55.90	-53.79
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	-32.65	-36.03	-37.75	-34.84
$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	-26.73	-28.71	-29.84	-27.43
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-20.11	-20.02	-19.76	-21.21
$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	-36.24	-39.01	-37.70	-38.63
$H + N_2 \rightarrow HN_2$	3.97	-0.07	1.58	-1.09
$H + CO \rightarrow HCO$	-19.51	-21.47	-20.27	-22.83
$H + C_2H_4 \rightarrow CH_3CH_2$	-40.03	-41.98	-41.20	-42.35
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	-26.12	-29.04	-28.48	-29.28
$HNC \rightarrow HNC$	15.05	13.22	13.35	13.16
$H + HCl \rightarrow H_2 + Cl$	-3.0	-1.08	-1.12	-0.49
$OH + H_2 \rightarrow H + H_2O$	-16.1	-16.75	-17.29	-16.55
$CH_3 + H_2 \rightarrow H + CH_4$	-3.2	-4.22	-4.35	-4.48
$OH + CH_4 \rightarrow CH_3 + H_2O$	-12.9	-12.53	-12.94	-12.07
$OH + NH_3 \rightarrow H_2O + NH_2$	-9.5	-9.87	-9.75	-9.71
$HCl + CH_3 \rightarrow Cl + CH_4$	-6.2	-5.29	-5.47	-4.98
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	-16.5	-17.16	-17.06	-16.40
$F + H_2 \rightarrow HF + H$	-31.6	-33.00	-33.29	-32.71
$O + CH_4 \rightarrow OH + CH_3$	5.6	4.46	5.13	4.53
$H + PH_3 \rightarrow PH_2 + H_2$	-20.1	-21.25	-21.37	-20.18
$H + HO \rightarrow H_2 + O$	-2.4	-0.25	-0.78	-0.05
$H + H_2S \rightarrow H_2 + HS$	-13.8	-12.87	-12.79	-12.25
$O + HCl \rightarrow OH + Cl$	-0.6	-0.83	-0.34	-0.45
$NH_2 + CH_3 \rightarrow CH_4 + NH$	-14.4	-12.76	-13.23	-12.76
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	-10.8	-8.13	-9.11	-8.43
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	-7.0	-7.29	-7.31	-6.69
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	-3.3	-2.66	-3.20	-2.37
MSE		-0.58	-0.86	-0.24
MAE		1.49	1.65	1.63
rms		1.79	2.29	2.06

TABLE XXII. Binding energies (in kcal/mol) of several sets of noncovalent interactions. The first three sets are taken from Ref. [92] with monomer deformation energies taken into considerations. The last three sets are taken from Ref. [64] without considering monomer deformation energies. The counter-point corrections are applied for all the cases.

Complex	ΔE_{ref}	ω M05-D	M05-2X	ω B97X-D
Charge-transfer complexes				
C ₂ H ₄ ...F ₂	1.06	0.79	1.00	0.78
NH ₃ ...F ₂	1.81	1.41	1.44	1.50
C ₂ H ₂ ...ClF	3.81	3.82	4.51	3.66
HCN...ClF	4.86	4.21	4.72	4.21
NH ₃ ...Cl ₂	4.88	4.61	5.02	4.81
H ₂ O...ClF	5.36	5.21	5.83	5.18
NH ₃ ...ClF	10.62	10.64	11.07	11.12
MSE		-0.24	0.17	-0.16
MAE		0.25	0.33	0.31
Dipole-dipole interaction complexes				
H ₂ S...H ₂ S	1.66	1.44	1.42	1.54
HCl...HCl	2.01	1.62	1.71	1.69
H ₂ S...HCl	3.35	3.26	3.23	3.38
CH ₃ Cl...HCl	3.55	3.08	3.24	3.17
HCN...CH ₃ SH	3.59	3.68	3.65	3.72
CH ₃ SH...HCl	4.16	4.82	4.84	4.87
MSE		-0.07	-0.04	0.01
MAE		0.32	0.28	0.28
Weak interaction complexes				
He...Ne	0.04	-0.02	0.04	0.00
He...Ar	0.06	-0.03	0.07	0.00
Ne...Ne	0.08	-0.03	0.07	-0.02
Ne...Ar	0.13	-0.02	0.13	-0.01
CH ₄ ...Ne	0.22	0.13	0.20	0.13
C ₆ H ₆ ...Ne	0.47	0.44	0.62	0.24
CH ₄ ...CH ₄	0.51	0.68	0.51	0.60
MSE		-0.05	0.02	-0.08
MAE		0.10	0.03	0.11
Hydrogen-bonded DNA base pairs				
G...A HB	-11.30	-12.63	-10.82	-13.48
C...G WC	-30.70	-31.42	-30.66	-32.45
G...C WC	-31.40	-31.34	-30.67	-32.28
MSE		-0.67	0.42	-1.60
MAE		0.70	0.42	1.60
Interstrand base pairs				
G...G IS	-5.20	-5.38	-4.80	-5.43
G...G IS	0.80	0.88	2.38	1.15
C...C IS	3.10	3.34	3.75	3.29
MSE		0.04	0.88	0.10
MAE		0.17	0.88	0.25
Stacked base pairs				
A...G S	-6.50	-6.84	-3.61	-6.66
C...G S	-12.40	-11.09	-8.57	-10.83
G...C S	-11.60	-11.26	-8.78	-11.06
MSE		0.44	3.18	0.65
MAE		0.66	3.18	0.76
MSE		-0.11	0.50	-0.15
MAE		0.31	0.61	0.43